THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R.

Volume 26, No. 5

May, 1956

(A Publication of the Academy of Sciences of the U.S.S.R.)

IN ENGLISH TRANSLATION

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227 West 17th Street
New York 11, N. Y.

Printed in the United States

Annual subscription	$ 175.00
Single issue	30.00

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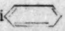
PHOTOCHEMICAL CHLORINATION OF PHENYLTRICHLOROSILANE

A. D. Petrov•, V. A. Ponomarenko, B. A. Sokolov and V. U. Roshal

Despite the fact that the action of chlorine and bromine on aromatic organosilicon compounds was studied long ago [1], chlorination and bromination of phenyltrichlorosilane were successfully carried out only very recently [2-5]. Yakubovich and Motsarev [3,4], who studied this problem in detail, showed that chlorination of phenyltrichlorosilane at temperatures of 50-125° in presence of Fe, $SbCl_3$, $AlCl_3$ and I_2 takes place with formation (depending on the reaction conditions and catalyst used) of mono- through pentachlorophenyltrichlorosilanes. $AlCl_3$, along with chlorination, also causes strong destruction of the initial $C_6H_5SiCl_3$. Diphenyldichlorosilane [3,4] and phenylmethyldichlorosilane [2] also chlorinate in approximately the same manner under these conditions. Utilization of metallic iron permits also the bromination of phenyltrichlorosilane to be carried out [6]. $C_6H_5SiCl_3$ is also brominated by liquid bromine in a stream of chlorine [5].

Also, prior to our work, it was not clear whether it was possible to carry out chlorination of phenyltrichlorosilane without using the above-cited catalysts; Yakubovich and Motsarev [3,4] were unable to chlorinate phenyl- and diphenyldichlorosilanes without catalysts even at 200°. Upon photochemical chlorination of diphenyldichlorosilane at 70°, attempts to prepare the chloro derivatives also failed [3]. The problem of the nature of the orienting effect of the trichlorosilyl group during chlorination of phenyltrichlorosilane was also insufficiently clear. In general, works devoted to the study of orientation in the benzene ring, when the directing substituent is $(CH_3)_3Si^{-}$, $(C_2H_5)_3Si^{-}$, $(C_6H_5)_3Si^{-}$, Cl_3Si^{-}, etc., are very few in number.

Kipping and Cusa [7], studying the nitration of phenylethylsilanes with nitric acid, noted the regular change of the meta orienting effect to an ortho-para orienting effect upon gradual replacement of more electronegative phenyl groups by less electronegative ethyl groups and transition from $(C_6H_5)_3Si$ to $(C_2H_5)_3Si$. The trimethylsilyl group, like copper nitrate [8] and nitric acid [9], also displays, although weakly, an ortho-para orienting effect during nitration of $(CH_3)_3Si$. Group $(C_2H_5)_3Si^{-}$ proved to be more weakly ortho-para orienting than the methyl group [10]. In contrast to the latter, the $SiCl_3$ group, as well as the $(C_6H_5)_3Si^{-}$ group exhibits a marked meta orienting effect during the nitration of Cl_3Si [3].

With regard to the chlorination and bromination reactions of phenyltrichlorosilane, although Yakubovich and Motsarev supposed that group $SiCl_3$ was meta orienting [3,4,6], under the conditions studied only the formation of p-chloro- (or bromo) phenyltrichlorosilanes took place. Yakubovich and Motsarev [3] explained the exclusive formation of para isomers by the effect of the catalysts used ($AlCl_3$, $SbCl_3$, $FeCl_3$, etc.) which formed adducts with phenyltrichlorosilane.

A study of the distinguishing characteristics of the chlorination of ethylsilane chlorides with sulfuryl chloride in presence of benzoyl peroxide, carried out by American investigators [11], and with chlorine with ultraviolet-light irradiation, carried out by us [12], showed that in the case of $Cl_3SiCH_2CH_3$ the trichlorosilyl group exhibits a definite and marked β-directing effect, since the quantity of β-chloroethyltrichlorosilane that forms

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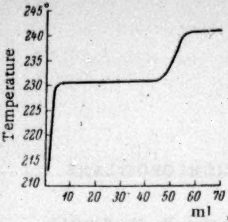
•To mark the occasion of the sixtieth birthday and 35th anniversary of the outstanding activity of Petrov Aleksandr Dmitrievich, Corresponding Member of the Academy of Sciences USSR, the Editorial Board of the "Journal of General Chemistry" publishes in this issue all the articles of A. D. Petrov that were received in 1955.

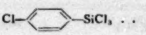
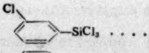
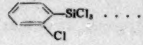


Sublimation curve of mixture of monochlorophenyltrichlorosilanes.

considerably exceeds the quantity of α-chloroethyltrichlorosilane; the β-directing effect of the $SiCl_3$ groups is apparent also during the chlorination of other compounds [13]. When β-chloroethyltrichlorosilane $Cl_3SiCH_2CH_2Cl$ is further chlorinated with SO_2Cl_2, only β,β-dichloroethyltrichlorosilane $Cl_3SiCH_2CHCl_2$ is formed [14]. In this respect the $SiCl_3$ group is similar to the CF_3 group, although the directing action of the latter is considerably more clearly expressed during the chlorination of $F_3CCH_2CH_3$ [15]. This is apparent from the fact that during the chlorination of 1,1,1-trifluoropropane, the hydrogens of the methyl group are first consecutively replaced by chlorine and only then the methylene group begins to chlorinate under harsher conditions.

If, with respect to effect on adjacent bonds, the CF_3 and $SiCl_3$ groups have something in common, it is natural to expect that also during chlorination of $F_3C-C_6H_5$ and $Cl_3Si-C_6H_5$ their effect should be approximately the same, i.e. as Yakubovich and Motsarev suggested and as it follows from the above-cited investigations, the $SiCl_3$ group should be meta orienting, although not so markedly as the CF_3 group.

In order to verify the correctness of this assumption, it was necessary to exclude the catalysts that Yakubovich and Motsarev used and create conditions under which the influence of the $SiCl_3$ group would not be so greatly complicated by other factors. We carried out chlorination of phenyltrichlorosilane at its boiling point in the apparatus that we described previously and which effected removal of the monochloro derivatives from the reaction zone during irradiation with ultraviolet light. As the sublimation curve for monochlorophenyltrichlorosilanes (figure) shows, a considerable quantity of chloro derivatives formed, the structure of which remained to be established.

Compound	Boiling point	Pressure (in mm)	d_4^{20}	n_D^{20}	MR_D	
					Found	Calculated
(I)  . . {	232.5° 100	745.5 11	1.4316	1.5418	54.00	53.83
(II) 	230.5	738	1.4384	1.5421	53.83	53.83
(III) 	240.5	742.5	1.4629	1.5510	53.64	53.83

A comparison of the properties of p-chlorophenyltrichlorosilane and m-chlorophenyltrichlorosilane, prepared by the Grignard reaction from the respective chlorobromobenzenes and $SiCl_4$, with the properties of the obtained monochlorides, showed that we dealt with a mixture of all three isomers. This comparison and also analysis via Raman spectra*, permitted the following to be established: 1) the fraction with b.p. 230-232° is a mixture of two isomers m- and p-chlorophenyltrichlorosilanes, 2) the fraction with b.p. 240.5° is an individual compound and has a spectrum that is sharply different from the spectra of the two other chlorophenyltrichlorosilanes; the mass of data leads us to conclude that this is pure o-chlorophenyltrichlorosilane; 3) the ratio between the o-, m- and p-chlorophenyltrichlorosilanes in the mixture is 20-25:55:20-25; if it is taken into account that a portion of the m- and p-chlorophenyltrichlorosilanes remained in the intermediate fraction upon distillation of $C_6H_5SiCl_3$, then the percentage of m-chlorophenyltrichlorosilane will be actually somewhat larger.

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*The quantitative analysis of the mixture of chlorophenyltrichlorosilanes was carried out by M. I. Batuev. We take the opportunity of expressing our deep appreciation to him.

Thus, the trichlorosilyl group really displays, although not very markedly, a meta orienting effect during chlorination of phenyltrichlorosilane at 200° with ultraviolet light irradiation.

In conclusion, it must be said that certain literature constants for p-chlorophenyltrichlorosilane [3,16] and, especially, for o-chlorophenyltrichlorosilane obtained during chlorination of $C_6H_5SiCl_3$ [17], cannot be considered accurate. The properties of the o-, m- and p-chlorophenyltrichlorosilanes that we obtained are given in the table.

EXPERIMENTAL

1. Chlorination of phenyltrichlorosilane was carried out with chlorine in the vapor phase under conditions that provided for the removal of the chlorination products from the reaction zone (previously described in [18]). 255 g phenyltrichlorosilane (b.p. 199-200° at 748 mm) was chlorinated for 42 hours until the temperature in the flask rose to 226°. Fractionation of the chlorination products on a 35-plate column yielded 93 g unreacted phenyltrichlorosilane and 137 g mixture of monochlorides (fraction with b.p. 228-240°). The yield of monochlorides on the reacted phenyltrichlorosilane was 83%. A repeated fractionation of the monochlorosilane mixture (figure) yielded pure o-chlorophenyltrichlorosilane (III).

Found %: C 29.45, 29.14; H 1.53, 1.58; Si 11.53, 11.19; Cl 56.84, 56.92. $C_6H_4SiCl_4$.
Calculated %: C 29.30; H 1.64; Si 11.41; Cl 57.65.

2. p-Chlorophenyltrichlorosilane (I). To 21.2 g magnesium in 150 ml absolute ether with stirring was added a solution of 166 g p-chlorobromobenzene* in 250 ml ether. The Grignard reagent was transferred to a dropping funnel and added dropwise with stirring to 250 g silicon tetrachloride in 150 ml ether. The reaction mixture was heated on a water bath for 8 hours. After separation of the precipitate and driving off the ether and $SiCl_4$, the product was vacuum fractionated. The isolated p-chlorophenyltrichlorosilane fraction weighed 51 g (yield 25%) and had b.p. 99-100° (11 mm). This fraction was fractionated two more times on a 35-plate column. Yield 43 g p-chlorophenyltrichlorosilane.

Found %: C 29.70, 29.65; H 1.83, 1.78; Si 11.17, 11.27; Cl 57.40, 57.37. $C_6H_4SiCl_4$.
Calculated %: C 29.30; H 1.64; Si 11.41; Cl 57.65.

3. m-Chlorophenyltrichlorosilane (II). To 16.5 g magnesium in 150 ml absolute ether with stirring was added 130 g m-chlorobromobenzene in 200 ml ether. m-Chlorobromobenzene (b.p. 194-195.5° at 751 mm) was prepared via the diazo compound from m-chloroaniline. The Grignard reagent was transferred to a dropping funnel and with stirring was added dropwise to 250 g silicon tetrachloride in 150 ml ether. The reaction mixture was heated on a water bath for 6 hours. After the precipitate was separated off, the ether and $SiCl_4$ driven off, and the residue distilled under vacuum, we obtained 68.5 g m-chlorophenyltrichlorosilane (yield 41.5%, b.p. 94.5-96.5° at 10 mm) which was twice fractionated on a 35-plate column. Yield 39 g m-chlorophenyltrichlorosilane.

Found %: C 29.29, 29.16; H 1.82, 1.87; Si 11.20, 11.39; Cl 57.24, 57.21. $C_6H_4SiCl_4$.
Calculated %: C 29.30; H 1.64; Si 11.41; Cl 57.65.

Attempts to prepare o-chlorophenyltrichlorosilane by the Grignard reaction from o-chlorobromobenzene via Mg, and also via Li, failed.

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*p-Chlorobromobenzene was prepared from chlorobenzene by bromination over iron filings. p-Chlorobromobenzene was taken for reaction, recrystallized 4 times from ethyl alcohol, m.p. 66.9-67.2°. Literature data [19] give m.p. 67°.

SUMMARY

1. It was established that phenyltrichlorosilane may be chlorinated photochemically.

2. It was found that under the conditions of photochemical chlorination of phenyltrichlorosilane at 200°, the trichlorosilyl group is weakly meta orienting.

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Received August 5, 1955

Institute of Organic Chemistry of
Academy of Sciences USSR

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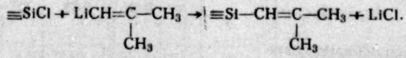
*T.p. = C. B. Translation pagination.

ORGANOLITHIUM SYNTHESIS AND PROPERTIES OF α- AND β- ALKENYLSILANES

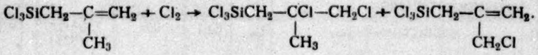
A. D. Petrov and G. I. Nikishin

Both mono- and polyalkenylsilanes with a multiple bond in the β-position are readily formed in high yields upon condensation of organomagnesium compounds with alkylchlorosilanes [1]. This route is not applicable for preparing α-alkenylsilanes. The synthesis of mono-α-alkenylsilanes is carried out either by a direct method [2] or by cleavage of HX from haloaklylsilanes with the halogen located in the alkyl chain [2,3]. For the preparation of poly-α-alkenylsilanes two methods have been suggested: that of the organosodium synthesis (first investigated by Kanasachi [4] and then developed by Petrov and Mironov), and that of the organolithium synthesis. Previously [5], we demonstrated the possibility of preparing α-alkenylsilanes, isopropenyltrimethylsilane (III), mono-, di-, tri- and tetraisocrotylsilanes (VI)-(X) (see table) according to scheme:



$$\equiv SiCl + LiCH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \rightarrow \equiv Si{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 + LiCl.$$

Moreover, we established [6] that isopropenyltrimethylsilane (III), upon reaction with hydrogen bromide, forms α-bromoisopropyltrimethylsilane and chlorination of methallyltrichlorosilane partially proceeds according to the anomalous scheme [7]:



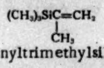
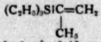
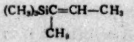
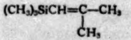
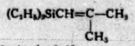
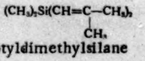
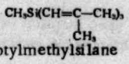
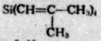
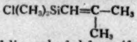
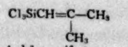
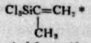
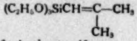
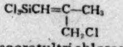
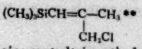
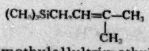
$$Cl_3SiCH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + Cl_2 \rightarrow Cl_3SiCH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}Cl{-}CH_2Cl + Cl_3SiCH_2{-}\underset{\displaystyle CH_2Cl}{\underset{|}{C}}{=}CH_2.$$

In the present work, which is a continuation of the cited investigations, the organolithium method of synthesis was used in order to prepare new representatives of the α-alkenyltrialkylsilanes and also of the α-alkenylchlorosilanes. The synthesis of α-alkenylchlorosilanes, which cannot be effected with sodium or magnesium as condensing agents, only needed a changed procedure, i.e. running in the components in the reverse order. Upon addition of isocrotyllithium to dimethyldichlorosilane and isocrotyllithium or isopropenyllithium to silicon tetrachloride, we obtained isocrotyldimethylchlorosilane (XI), isocrotyltrichlorosilane (XII) and isopropenyltrichlorosilane (XIII):

$$SiCl_4 + LiCH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \rightarrow Cl_3SiCH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 + LiCl\ .$$

The organolithium synthesis of the β-alkenylsilane, γ,γ-dimethylallyltrimethylsilane (XVII), proceeded according to the equation

$$(CH_3)_3SiCH_2Li + BrCH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \rightarrow \underset{(XVII)}{(CH_3)_3SiCH_2CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3} + LiCl.$$

No.	Unsaturated organosilicon compounds	Molar ratio of components			Boiling point (mm)	d_4^{20}	n_D^{20}
		Li	RBr	organo-silicon compound			
(I)	$(CH_3)_3SiCH{=}CH{-}CH_3$ propenyltrimethylsilane	0.88	0.43	0.27	86—87° (754)	0.7167	1.4086
(II)	$(C_2H_5)_3SiCH{=}CH{-}CH_3$ propenyltriethylsilane	1.43	0.7	0.31	166.5—169.5° (746)	0.7814	1.4441
(III)	 $(CH_3)_3SiC(CH_3){=}CH_2$ isopropenyltrimethylsilane	2	1	0.6	82.8—83° (746)	0.7186	1.4070
(IV)	 $(C_2H_5)_3SiC(CH_3){=}CH_2$ isopropenyltriethylsilane	0.64	0.4	0.2	163—163.5° (742)	0.7878	1.4430
(V)	 $(CH_3)_3SiC(CH_3){=}CH{-}CH_3$ α-methylpropenyltrimethylsilane	1.2	0.63	0.32	112—113.5° (747)	0.7543	1.4283
(VI)	 $(CH_3)_3SiCH{=}C(CH_3){-}CH_3$ isocrotyltrimethylsilane	2	1.2	0.5	111.5—112° (746)	0.7418	1.4250
(VII)	 $(C_2H_5)_3SiCH{=}C(CH_3){-}CH_3$ isocrotyltriethylsilane	1	0.48	0.25	185—186° (740)	0.7976	1.4538
(VIII)	 $(CH_3)_2Si(CH{=}C(CH_3){-}CH_3)_2$ diisocrotyldimethylsilane	1.3	0.74	0.29	168—170° (763)	0.7956	1.4590
(IX)	 $CH_3Si(CH{=}C(CH_3){-}CH_3)_3$ triisocrotylmethylsilane	1.2	0.81	0.15	221—222.5° (750)	0.8262	1.4820
(X)	 $Si(CH{=}C(CH_3){-}CH_3)_4$ tetraisocrotylsilane	1.9	1.4	0.12	m.p. 54.5		
(XI)	 $Cl(CH_3)_2SiCH{=}C(CH_3){-}CH_3$ isocrotyldimethylchlorosilane	1.2	0.61	0.6	136—137° (735)	0.9092	1.4430
(XII)	 $Cl_3SiCH{=}C(CH_3){-}CH_3$ isocrotyltrichlorosilane	1.28	0.66	0.88	152—153° (743)	1.1968	1.4586
(XIII)	 $Cl_3SiC(CH_3){=}CH_2$ * isopropenyltrichlorosilane	1.5	0.7	0.9	114—115° (750)	—	1.4428
(XIV)	 $(C_2H_5O)_3SiCH{=}C(CH_3){-}CH_3$ isocrotyltriethoxysilane	0.8	0.5	0.4^{8}	184—185° (750)	0.8988	1.4221
(XV)	 $Cl_3SiCH{=}C(CH_2Cl){-}CH_3$ γ-chloroisocrotyltrichlorosilane				179—180° (750)	1.3320	1.4802
(XVI)	 $(CH_3)_3SiCH{=}C(CH_2Cl){-}CH_3$ ** γ-chloroisocrotyltrimethylsilane				155—156° (745)	0.9116	1.4534
(XVII)	 $(CH_3)_3SiCH_2CH{=}C(CH_3){-}CH_3$ γ,γ-dimethylallyltrimethylsilane	0.5	0.37	0.32	132—132.3° (739)	0.7549	1.4290

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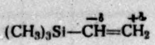
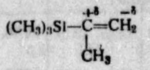
*Previously prepared by Sommer and Evans [10] via the dehydrochlorination of β-chloroisopropyltrichlorosilane by quinoline.

** Found %: Cl 21.60, 21.14. Calculated %: Cl 21.79.

MR_D		Yield (%)	Found (%)			Gross formula	Calculated (%)		
found	calculated		C	H	Si		C	H	Si
39.37	39.42	30	62.78, 62.63	12.48, 12.37	24.90, 24.86	$C_6H_{14}Si$	63.16	12.35	24.50
53.13	52.95	36.2	69.59, 69.76	12.92, 12.80	17.50, 17.13	$C_9H_{20}Si$	69.20	12.90	17.90
39.13	39.07	43	63.64, 63.69	12.55, 12.52	24.00, 23.67	$C_6H_{14}Si$	63.16	12.35	24.50
52.58	52.60	40	69.96, 69.90	13.00, 13.00	17.59, 17.37	$C_9H_{20}Si$	69.20	12.90	17.90
43.74	43.70	44.6	65.41, 65.51	12.47, 12.43	21.76, 22.00	$C_7H_{16}Si$	65.54	12.57	21.90
44.20	44.15	64	65.46, 65.19	12.70, 12.09	21.10, 21.07	$C_7H_{16}Si$	65.54	12.57	21.90
57.80	57.68	70	71.13, 71.24	12.45, 12.70	16.43, 16.51	$C_{10}H_{22}Si$	70.51	13.01	16.47
57.83	58.02	43	70.42, 70.70	11.77, 11.94	16.89, 16.92	$C_{10}H_{20}Si$	71.36	11.97	16.67
71.90	71.89	37.2	74.70, 74.80	11.46, 11.66	—	$C_{15}H_{24}Si$	75.02	11.01	—
			77.28, 77.01	11.04, 11.14	11.84, 11.90	$C_{18}H_{28}Si$	77.34	11.36	11.29
43.35	43.78	40	48.52, 48.45	8.74, 8.96	—	$C_6H_{13}SiCl$	48.47	8.82	—
43.25	43.04	27.3	25.68, 25.62	3.74, 3.54	—	$C_4H_7SiCl_3$	25.38	3.72	—
—	—	—	—	—	—	$C_3H_5SiCl_3$	—	—	—
—	—	1.5	—	—	—	$C_{10}H_{22}O_2Si$	—	—	—
47.75	47.43	27.8	—	—	—	$C_4H_6SiCl_4$	—	—	—
48.26	48.54	20	51.30, 51.31	8.89, 9.08	17.19, 16.84	$C_7H_{15}ClSi$	51.67	9.29	17.24
48.59	48.33	36.2	66.33, 66.36	12.71, 12.73	19.67, 19.86	$C_8H_{18}Si$	67.53	12.74	19.72

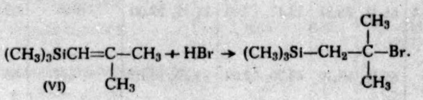
The properties and yields of the obtained compounds and also the molar ratios of the components of the reaction are given in the table. Upon chlorination of isocrotyltrichlorosilane (XII), the yield of the γ-chloroisocrotyltrichlorosilane (XV) that formed was 27%.





In contrast to $(CH_3)_3Si-\overset{-\delta}{CH}=\overset{+\delta}{CH_2}$ in $(CH_3)_3Si-\underset{CH_3}{\overset{+\delta}{C}}=\overset{-\delta}{CH_2}$ the shifting of the electron density of the π-bond occurs in another direction. This is reflected in a different order of addition of HBr to these two compounds (HBr adds to vinyltrimethylsilane in violation of the Markovnikov rule and to isopropenyltrimethylsilane in accordance with the rule [6,8]) and, probably, this is due to the predominant effect of the α-methyl group over the trimethylsilyl group (σπ-conjugation of the C = C-bond and C–H-bonds of the α-methyl group).

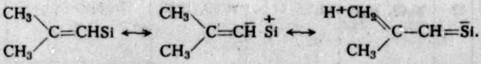
In isocrotyltrimethylsilane (VI) the effect of the trimethylsilyl group and the effect of the methyl groups of the isocrotyl radical orient the addition of HBr in another direction [5]:



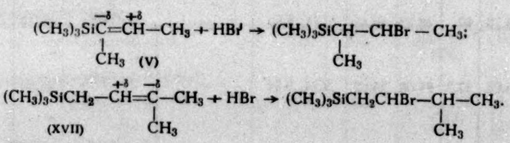
$$(CH_3)_3SiCH=\underset{CH_3}{C}-CH_3+HBr\rightarrow(CH_3)_3Si-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Br.$$

(VI)

The explanation of Kanasachi of this result in terms of the resonance of three structures therefore seems quite superfluous [8]:



In the present investigation the addition of hydrogen bromide to α-methylpropenyltrimethylsilane (V) and γ,γ-dimethylallyltrimethylsilane (XVII) was studied:



$$(CH_3)_3Si\underset{CH_3}{\overset{-\delta}{C}}=\overset{+\delta}{CH}-CH_3+HBr\rightarrow(CH_3)_3Si\underset{CH_3}{CH}-CHBr-CH_3;$$

(V)

$$(CH_3)_3SiCH_2-\overset{+\delta}{CH}=\underset{CH_3}{\overset{-\delta}{C}}-CH_3+HBr\rightarrow(CH_3)_3SiCH_2CHBr-\underset{CH_3}{CH}-CH_3.$$

(XVII)

In the first case the effects of the methyl groups at the α- and β-carbon atoms balance each other out and, hence, the reason for the addition of HBr here, as in vinylsilanes, being against the Markovnikov rule, is quite understandable. In our opinion, the addition of HBr against the Markovnikov rule is less clear in the second case despite the presence of methyl groups at the γ-carbon atom that direct addition according to the rule. However, this fact also may be explained by the conjugation of Si–C- and C=C-bonds and the high degree of polarization of the C=C-bond under the influence of the $(CH_3)_3Si$ group. Only the formation of trimethylbromosilane, as the basic product separated upon vacuum distillation of the reaction mixture, indicates the cited order of addition. This fact does not permit us to consider the order of addition to be strictly confirmed.

EXPERIMENTAL

Synthesis of α-alkenylsilanes. All the α-alkenylsilanes (I-XIV) given in the table were prepared by one method. In the case of α-alkenylchlorosilanes and isocrotyltriethoxysilane, only the order of introduction into the reaction of the components was changed, namely, the lithiumalkenyls were added to $SiCl_4$, $(CH_3)_2SiCl_2$ and $(C_2H_5O)_4Si$.

We present a typical description of the synthesis of α-methylpropenyltrimethylsilane (V). To 8.4 g (1.2 mole) finely divided metallic lithium in 300 ml ether, in order to initiate the reaction, was added 5 ml 2-bromo-2-butene from a total weighed quantity of 75 g (0.63 mole). The remaining bromide was added dropwise with vigorous stirring for $3\frac{1}{2}$ hours. Then 35 g (0.32 mole) trimethylchlorosilane was added. After standing overnight, the reaction mass was filtered from the unreacted lithium and decomposed with water. By the usual procedure, 18.5 g of product was separated from the ethereal solutions. The synthesis was carried out in an atmosphere of nitrogen. The properties of the product are given in the table.

Synthesis of γ,γ-dimethylallyltrimethylsilane (XVII). As in the preceding synthesis, after the start of the reaction, to 5.3 g (0.75 mole) lithium in 300 ml ether in the course of 2 hours was added 39.5 g (0.32 mole) chloromethyltrimethylsilane. To the ethereal solution of the organolithium compound, after freeing it from unreacted lithium, was added 50 g (0.37 mole) isocrotyl bromide. The ether was then partially driven off; the reaction mass was heated for 2 hours at 50° and decomposed with water. From the ethereal solution was isolated 16.6 g of product, the properties of which are given in the table.

Addition of hydrogen bromide to isopropenyltrimethylsilane (III), α-methylpropenyltrimethylsilane (V) and γ,γ-dimethylallyltrimethylsilane (XVII). Hydrogen bromide began to bubble through the silicoolefins at 20-22°. After the temperature of the liquid had risen 2-3°, the vessel with the weighed sample was placed in a freezing mixture and the reaction continued at –70°. In all cases HBr added very vigorously (for 10-20 minutes).

A. Hydrogen bromide was bubbled through 18 g (0.158 mole) of isopropenyltrimethylsilane (III) until a weight addition of 8.5 g (theoretical weight addition 12.8 g). The crystals that formed prohibited further bubbling of HBr through the reaction mass. After separation from the liquid and sublimation, the crystals were white, had the odor of alkyl bromides and m.p. 124°. They were sticky, waxy, smeared on glass, withstood heating up to 130° without decomposing, did not react with 0.1 N alkali and methyllithium at the boiling point of ether. Yield 40%.

B. Through 8.6 g (0.067 mole) α-methylpropenyltrimethylsilane (V) was passed hydrogen bromide until a weight addition of 6.2 g (theoretical weight addition 5.5 g). The α-methyl-β-bromopropyltrimethylsilane which formed distilled without decomposition at 65-66° (18 mm) and had the following properties: d_4^{20} 1.1132, n_D^{20} 1.4618, MR_D 51.64; calc. 51.85. Yield 50% (7.1 g). Treatment of 6.8 g β-bromide with 0.1 N KOH yielded 1.2 g (55%) hexamethyldisiloxane with b.p. 100-103°, n_D^{20} 1.3785.

Literature data [9]: b.p. 98-100°, n_D^{20} 1.3771.

C. Through 8.8 g (0.0618 mole) γ,γ-dimethylallyltrimethylsilane (XVII) HBr was passed until the theoretical weight addition of 5 g was attained. Vacuum distillation of the reaction mixture yielded only 7.1 g (75.3% trimethylbromosilane (b.p. 81-82° at 747 mm) which, upon treatment with 0.1 N KOH, was converted to hexamethyldisiloxane with b.p. 100-102°, n_D^{20} 1.3794. Yield 41.6%.

Chlorination of isocrotyltrichlorosilane (XII) (80 g, 0.42 mole) was carried out with ultraviolet illumination until the temperature rose to 185° (8 hours). Fractionation of the reaction mixture yielded 2.5 ml of a fraction that boiled in the range of 50-75°, 11 g unreacted isocrotyltrichlorosilane and 22.6 g γ-chloroisocrotyltrichlorosilane (XV) (its properties are given in the table). The residue, more than 50 g, was a viscous brown resin. The yield of the product of anomalous chlorination was 27.8%, calculated on the reacted isocrotyltrichlorosilane.

Methylation of γ-chloroisocrotyltrichlorosilane (XV). A Grignard reagent was prepared in ether from 10 g (0.41 mole) magnesium and a corresponding quantity of methyl chloride. To this was added 21 g (0.11 mole) (XV), after which the reaction mass was boiled for 10 hours and then decomposed with water. 4.5 g of product (XVI) was separated from the ethereal solution, the properties of which are given in the table. On the basis of a study of the Raman spectrum of γ-chloroisocrotyltrimethylsilane, which lacks frequencies in the region 3000-3100 cm^{-1}, characterizing a terminal multiple bond, the above-described structure of the chlorination product may be considered true. This conclusion is also substantiated by material on the chlorination of the propyl-, isobutyl- and methallyltrichlorosilanes. In these three cases the α-chloride either is not obtained at all or is obtained in negligible quantity.

SUMMARY

1. It was shown that the organolithium method of synthesis yields mono- and poly-α-alkenylalkylsilanes as well as α-alkenylchlorosilanes.

2. Anomalous chlorination of isocrotyltrichlorosilane, analogous to the anomalous chlorination of methallyltrichlorosilane and isobutylene, was carried out.

3. It was established that hydrogen bromide adds to α-methylpropenyltrimethylsilane and γ,γ-dimethylallyltrimethylsilane in violation of the Markovnikov rule.

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Received September 5, 1955

Institute of Organic Chemistry of Academy
of Sciences USSR

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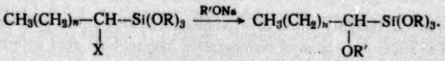
*T.p. = C. B. Translation pagination.

SYNTHESIS OF SILICON-CONTAINING ETHERS AND DIETHERS

S. I. Sadykhzade, I. I. Tsetlin and A. D. Petrov

In contrast to siloxanes and alkoxysilanes, ethers with the silicon atom in the α-, β- and γ-positions with respect to the ether bond have been studied very little. Ethers with a silicon atom located at the α-carbon with respect to the ether bond have been prepared [1] according to the equation:



$$CH_3(CH_2)_n-\underset{X}{\underset{|}{C}H}-Si(OR)_3 \xrightarrow{R'ONa} CH_3(CH_2)_n-\underset{OR'}{\underset{|}{C}H}-Si(OR)_3.$$

Ethers with the silicon atom located at the β- and γ-carbons were recently synthesized [2] according to the schemes:

$$HSiCl_3 + CH_2{=}CH-OC_2H_5 \rightarrow Cl_3Si-CH_2-CH_2OC_2H_5,$$
$$HSiCl_3 + CH_2{=}CH-CH_2OCH_3 \rightarrow Cl_3Si-CH_2-CH_2-CH_2-OCH_3.$$

In contrast to silicon-containing ketones and acids, for the synthesis of which the organomagnesium method has been very widely used [3] in the synthesis of ethers, this method has still not been employed. In the present investigation, ethers with the silicon atom in the β-, γ- and δ-positions with respect to the ether bond were prepared by us via organomagnesium synthesis, both by the Grignard and by the Barbye-Yavorsky schemes.*

It was established that the yields of the synthesis products in each of these methods vary in a very broad range depending on the structure of the condensed compounds.

Barbye-Yavorsky scheme

$$(R)_3SiX + Mg + ClCH_2CH_2CH_2OCH_3 \rightarrow (R)_3SiCH_2CH_2CH_2OCH_3$$

yielded the following compounds:

(I) $(CH_3)_3SiCH_2CH_2CH_2OCH_3$ (yield 68%),

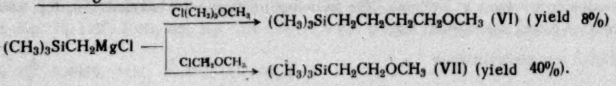
(II) $(C_2H_5)_3SiCH_2CH_2CH_2OCH_3$ (yield 7.2%)),

(III) $(CH_3)_2(C_2H_5)SiCH_2CH_2CH_2OCH_3$ (yield 50%),

(IV) $(CH_3)_2Si(CH_2CH_2CH_2OCH_3)_2$ (yield 36%),

(V) $Cl_3SiCH_2CH_2CH_2OCH_3$ (yield 23.5%).

The Grignard scheme was used for (VI) and (VII).

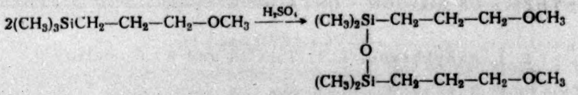


$$(CH_3)_3SiCH_2MgCl \xrightarrow{Cl(CH_2)_3OCH_3} (CH_3)_3SiCH_2CH_2CH_2CH_2OCH_3 \text{ (VI) (yield 8\%)}$$
$$(CH_3)_3SiCH_2MgCl \xrightarrow{ClCH_2OCH_3} (CH_3)_3SiCH_2CH_2OCH_3 \text{ (VII) (yield 40\%)}.$$

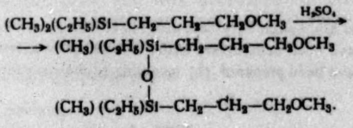
---

*We turned to this method of synthesis after having been convinced that $ClCH_2CH_2CH_2OCH_3$ does not enter into a direct synthesis and $Cl_3SiCH_2CH_2CH_2OCH_3$ cannot be prepared via this simple method.

The reason for the difference in yields evidently lies in the different condensation rates of the studied halides. Thus, for example, in preparing (II), the yield of which was small, very little triethylchlorosilane reacted, as the result of which hexaethylsiloxane separated out after hydrolysis. Let us observe that, in contrast to the cited primary γ-alkoxy halide, the secondary γ-alkoxy halide (2-chloro-4-methoxybutane) did not give the Grignard reagent upon reaction with magnesium but split out HCl, forming δ-methallylmethyl ether $CH_3-CH=CH-CH_2OH_3$. From ethers (I) and (III) the Sommer reaction [4] yielded diether siloxanes:



$$2(CH_3)_3SiCH_2-CH_2-CH_2-OCH_3 \xrightarrow{H_2SO_4} \begin{array}{l}(CH_3)_2Si-CH_2-CH_2-CH_2-OCH_3\\ \quad\;\; |\\ \quad\;\; O\\ \quad\;\; |\\ (CH_3)_2Si-CH_2-CH_2-CH_2-OCH_3\end{array} \qquad (VIII)$$



$$\begin{array}{l}(CH_3)_2(C_2H_5)Si-CH_2-CH_2-CH_2OCH_3 \xrightarrow{H_2SO_4}\\ \longrightarrow (CH_3)(C_2H_5)Si-CH_2-CH_2-CH_2OCH_3\\ \qquad\qquad\qquad\quad |\\ \qquad\qquad\qquad\quad O\\ \qquad\qquad\qquad\quad |\\ \qquad (CH_3)(C_2H_5)Si-CH_2-CH_2-CH_2OCH_3.\end{array} \qquad (IX)$$

A study was carried out on the stability of the Si–C bond on prepared ethers with respect to different reagents. The results showed that under the action of concentrated hydrochloric acid with heating, or of aluminum chloride at room temperature, the Si–C bond in γ-silicon ethers does not rupture; heating with $AlCl_3$ at 50-60° causes cleavage of the Si–C bond with formation of $(CH_3)_3SiCl$. The action of bromine on α-trimethylsilyl-γ-methoxypropane also led to the formation of trimethylbromosilane.

EXPERIMENTAL

γ-Chloropropylmethyl ether was prepared according to [5] from 1-chloro-3-bromopropane and was distilled on a column:

B.p. 110.2° at 734 mm, d_4^{20} 0.9971, n_D^{29} 1.4133, MR_D 27.29; calc. 27.14. According to [5] b.p. 116-118°.

α-Trimethylsilyl-γ-methoxypropane (I). In a 3-necked flask fitted with mechanical stirrer, reflux condenser and dropping funnel, were placed 350 ml absolute ether and 30 g magnesium. 0.5 g $AlCl_3$ was added as catalyst for the start of the reaction. A mixture was then added which consisted of 108.5 g γ-chloropropylmethyl ether and 108.5 g trimethylchlorosilane. The reaction goes with evolution of heat but cooling was not needed. After addition of the mixture, the contents of the flask were heated with stirring for 5 hours on a water bath and set aside overnight. The reaction mixture was treated as usual. The ethereal layer that separated out was dried over calcium chloride. After driving off the ether, the residue was subjected to fractionation on a column at 746 mm. The first fraction boiled up to 142.0°, 5.6 g; second fraction had b.p. 142.0°, 99.0 g; residue 10.5 g. The second fraction was α-trimethylsilyl-γ-methoxypropane (I):

d_4^{20} 0.7907, n_D^{20} 1.4112, MR_D 45.90; calc. 45.94.
Found %: C 58.09, 58.20; H 12.08, 12.36; Si 18.54, 18.95. $C_7H_{18}OSi$.
Calculated %: C 57.46; H 12.39; Si 19.31.

α-Triethylsilyl-γ-methoxypropane (II). To 8 g magnesium in 100 ml absolute ether and 0.3 g $AlCl_3$ was added a mixture consisting of 30 g α-chloro-γ-methoxypropane and 38 g triethylchlorosilane. The reaction was carried out in the main as in the preceding synthesis. After driving off the ether, the residue was subjected to fractionation on a column at 746 mm. The following fractions were isolated: 1st, b.p. 154-156°, 18 g; 2nd, b.p. 156-206.5°, 5 g; 3rd, b.p. 207.0°, 3 g.

The 1st fraction was triethylsilanol:

n_D^{20} 1.4370, d_4^{20} 0.8652; as per [6] b.p. 70.5° at 18 mm, n_D^{20} 1.4363, d_4^{20} 0.8637.

The 3rd fraction with b.p. 207° was α-triethylsilyl-γ-methoxypropane (II):

d_4^{20} 0.8375, n_D^{20} 1.4413, MR_D 59.43; calc. 59.83.
Found %: C 64.59, 64.73; H 12.46, 12.64; Si 13.67, 13.34. $C_{10}H_{24}OSi$.
Calculated %: C 63.50; H 12.76; Si 14.80.

Dimethylethyl-γ-methoxypropylsilane (III). The reaction was carried out as described above.

B.p. 164.0° at 752 mm, d_4^{20} 0.8059, n_D^{20} 1.4211, MR_D 50.44; calc. 50.59.
Found %: C 59.93, 59.85; H 12.49, 12.65; Si 17.56, 17.38. $C_8H_{20}OSi$.
Calculated %: C 59.95; H 12.56; Si 17.47.

Dimethyl-γ-dimethoxydipropylsilane (IV). The reaction was carried out as described above.

B.p. 105-106° at 20 mm, d_4^{20} 0.8676, n_D^{20} 1.4330, MR_D 61.20; calc. 61.60.
Found %: C 58.62, 58.60; H 11.90, 11.76; Si 13.72, 13.46. $C_{10}H_{24}O_2Si$.
Calculated %: C 58.77; H 11.84; Si 13.70.

Trichloro-γ-methoxypropylsilane (V). In a flask was taken 34.0 g magnesium, 250 ml absolute ether and 0.5 g $AlCl_3$. With stirring 108.5 g α-chloro-γ-methoxypropane was added dropwise. The prepared Grignard reagent was added to 85 g $SiCl_4$ dissolved in 100 ml absolute ether. The reaction mixture was heated on a water bath for 5 hours. The resulting precipitate was filtered off and washed with absolute ether. After driving off the ether, the filtrate was fractionated on a column. Yield 23.8 g of product.

B.p. 172.5° at 744 mm, n_D^{20} 1.4421, d_4^{20} 1.2272, MR_D 44.75; calc. 44.33.
Found %: C 23.13, 22.99; H 4.43, 4.58; Si 13.50, 13.50; Cl 50.65, 51.02. $C_4H_9OSiCl_3$.
Calculated %: C 23.14; H 4.37; Si 13.51; Cl 50.23. [2] gives b.p. 159° (756 mm), n_D^{20} 1.4420, d_4^{20} 1.2160.

α-Trimethylsilyl-β-methoxyethane (VII). In a 3-necked 0.5-liter flask was placed 8 g magnesium and 150 ml absolute ether; with stirring was added 28 g α-chloromethyltrimethylsilane. To the Grignard reagent which formed was then added 22 g methoxychloromethane; the reaction proceeded very vigorously with evolution of heat. The reaction mixture was heated for 5 hours on a water bath and treated as usual. After driving off the ether, the residue was fractionated in vacuum (70 mm). The following fractions were separated: 1st, b.p. 23-46°, 2.0 g; 2nd, b.p. 46-48°, 2.0 g; 3rd, b.p. 48-49°, 12 g; the 3rd fraction was α-trimethyl-β-methoxyethane (VII).

n_D^{20} 1.4030, d_4^{20} 0.7867, MR_D 41.31; calc. 40.99.
Found %: C 54.85, 54.35; H 12.16, 12.09; Si 21.37, 21.62. $C_6H_{16}OSi$.
Calculated %: C 54.55; H 12.12, Si 21.21.

α-Trimethylsilyl-δ-methoxybutane (VI). The reaction was carried out under the conditions of the preceding synthesis.

B.p. 59° at 15 mm, d_4^{20} 0.8213, n_D^{20} 1.4243, MR_D 49.83; calc. 50.56.

Diether siloxane (VIII). In a 100-ml conical flask was placed 12 g α-trimethylsilyl-γ-methoxypropane (I); then with stirring was slowly added 20 ml concentrated H_2SO_4; bubbles of gas then separated out. After stirring for 10 hours, the reaction mixture was poured into a flask with ice and extracted with ether. The extract was washed with 5% soda solution, water, and dried over $CaCl_2$. After driving off the ether, the residue was vacuum fractionated (10 mm) and the following fractions were collected: 1st, b.p. 69-73°, 3 ml; 2nd, b.p. 73-75°, 3 ml; 3rd, b.p. 75-122°, 1 ml; 4th, b.p. 122-124°, 3.5 ml; the 4th fraction was diether siloxane (VIII).

n_D^{20} 1.4253, d_4^{20} 0.8896, MR_D 80.10; calc. 80.24.
Found %: C 51.77, 51.56; H 11.06, 10.85; Si 20.30. $C_{12}H_{30}O_3Si_2$.
Calculated %: C 51.75; H 10.91; Si 20.12.

Diether siloxane (IX) was prepared by treatment of dimethylethyl-γ-methoxypropylsilane (III) with concentrated H_2SO_4.

B.p. 128-130° at 7 mm, d_4^{20} 0.8943, n_D^{20} 1.4312, MR_D 88.75; calc. 89.50.
Found %: C 53.97, 53.77; H 11.09, 11.19; Si 19.23, 19.42. $C_{14}H_{34}O_3Si_2$.
Calculated %: C 54.85; H 11.11; Si 18.36.

SUMMARY

1. The organomagnesium synthesis of silicon-containing ethers and diethers was effected for the first time by condensation of trialkylsilane chlorides with primary alkoxychloroalkanes.

2. It was shown that secondary alkoxychloroalkanes cannot enter into this synthesis.

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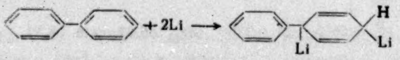
Received September 9, 1955

Institute of Organic Chemistry of the
Academy of Sciences of USSR

REACTION OF 1,4-DILITHIUMDIHYDRODIPHENYL WITH ALKYL HALIDES

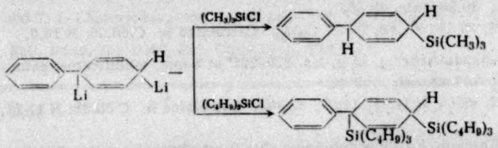
E. P. Kaplan, Z. I. Letina and A. D. Petrov

In a number of works [1-3] it was shown that metallic lithium readily adds to aromatic polynuclear hydrocarbons such as diphenyl, naphthalene, anthracene, phenanthrene, etc. Addition of lithium to diphenyl takes place according to the following scheme:



1,4-Dilithiumdihydrodiphenyl has hardly been used in the Wurtz reaction, although it would appear that via its alkylation it would be easy to obtain, for example, the as yet undescribed (in the literature) 1,4-dialkyldihydrodiphenyls.

A. D. Petrov and T. I. Chernysheva [4] carried out condensation reactions of 1,4-dilithium-1,4-dihydrodiphenyl with trimethylchlorosilane and with tributylchlorosilane. In the first case only monotrimethyldisilyldiphenyl was obtained and in the second, ditributylsilyldiphenyl:



In the present investigation we carried out Wurtz reactions of 1,4-dilithium-1,4-dihydrodiphenyl with n-hexyl and n-nonyl bromides, sec-octyl bromide and 2-ethylhexyl bromide. In all syntheses both the mono- and dialkylhydrodiphenyls were isolated; the yields of the former, as a rule, were twice as great. It is interesting to note that 4-alkyl-1,4-dihydrodiphenyls congealed at higher temperatures as crystals,while 1,4-dialkyl-1,4-dihydrodiphenyls with higher molecular weights congealed at considerably lower temperatures and often as vitreous masses. [For example, 4-hexyl-1,4-dihydrodiphenyl had solidification point +7° (crystals), 1,4-dihexyl-1,4-dihydrophenyl, −35° (glass); 4-n-nonyl-1,4-dihydrodiphenyl, m.p. +28°, 1,4-di-n-nonyl-1,4-dihydrodiphenyl, solidification point −2° (crystals)]. The cited phenomenon, evidently, is due to the fact that 4-alkyl-1,4-dihydrodiphenyls have a linear chain structure while 1,4-dialkyl-1,4-dihydrodiphenyls are similar to the hydrocarbons of so-called T-shaped structure which were noted on several occasions [5] to have low solidification points, being lower the longer the side chain, within certain limits.

Since the alkyl halides that we took had a relatively large molecular weight and in a number of cases a branched structure also, it was difficult to gauge the yield of lithium derivatives of diphenyl. Therefore, we carried out a synthesis experiment with dimethyl sulfate under analogous conditions with experiments on anthracene. The results of the synthesis showed that the yield of dimethyldihydrodiphenyl was equal to 60%, i.e., the addition of lithium to diphenyl was no less than 60%.

EXPERIMENTAL

Addition of lithium to diphenyl and further reactions were carried out under the following conditions. Into a 1-liter bottle was placed diphenyl, absolute ether or a mixture of ether and benzene, and glass beads. The air was displaced from the reaction vessel by a stream of dry nitrogen, and finely pulverized lithium was added. The bottle was stoppered and shaken on an agitator for 50-100 hours. On completion of the reaction, the vessel was connected with a double-branched adapter,in one end of which was placed a dropping funnel; through the other end the gases from the bottle exited. The reaction bottle was placed in a bath with ice water, and through the dropping funnel, with shaking, was added an ethereal solution of alkyl halide. When introduction of alkyl halide was complete, the reaction mixture was shaken for 3-4 hours more at room temperature, after which the unreacted lithium was separated off by filtration through glass wool. The ethereal solution was washed with water and dried. The solvent, the unreacted alkyl halide and diphenyl were then driven off, and the obtained alkylbiphenyls were vacuum fractionated.

Reaction of 1,4-dilithium-1,4-dihydrodiphenyl with dimethyl sulfate. For the reaction were taken 30 g diphenyl, 300 ml ether, and 3.5 g lithium. Shaking was carried out for 100 hours. The obtained dilithiumdihydrodiphenyl immediately ignited upon evaporating the ether. In the course of 2 hours 70 g dimethyl sulfate in 100 ml ether was added. 30 g dimethyl sulfate was driven off. Yield 20 g 4-methyl-1,4-dihydrodiphenyl.

B.p. 110-112° at 3 mm, n_D^{20} 1.5605, d_4^{20} 0.9758, MR_D 56.37; calc. 56.71.

The product is possibly a mixture of 4-methyl-1,4-dihydrodiphenyl with 1,4-dimethyl-1,4-dihydrodiphenyl.

Found %: C 91.54, 91.60; H 8.27, 8.32. $C_{13}H_{14}$. Calculated %: C 91.76; H 8.23.

Reaction of 1,4-dilithium-1,4-dihydrodiphenyl with n-hexyl bromide. For the reaction were taken 77 g diphenyl, 400 ml ether, 200 ml benzene, and 7 g lithium. Shaking was carried out for 60 hours. 120 g n-hexyl bromide was added. A total of 50 g product was obtained. Three fractional distillations yielded:

4-Hexyl-1,4-dihydrodiphenyl, 35 g, b.p. 199-200° at 5 mm, solidification point 7° (crystals), n_D^{20} 1.5484, d_4^{20} 0.9435, MR_D 80.85; calc. 79.86.
Found %: C 90.25, 90.19; H 9.98, 9.82. $C_{18}H_{24}$. Calculated %: C 90.00; H 10.0.

1,4-Dihexyl-1,4-dihydrodiphenyl, 15 g, b.p. 220-221° at 5 mm, solidification point -35° (glass), n_D^{20} 1.5248, d_4^{20} 0.9241, MR_D 107.42; calc. 107.73.
Found %: C 88.67, 88.63; H 11.16, 11.37. $C_{24}H_{36}$. Calculated %: C 88.88; H 11.11.

Reaction of 1,4-dilithium-1,4-dihydrodiphenyl with 2-ethylhexyl bromide. For the reaction were taken 77 g diphenyl, 400 ml ether, 200 ml benzene, and 7 g lithium. Shaking was carried out for 70 hours. 130 g 2-ethylhexyl bromide was added. Yield 40 g alkylbiphenyls. Fractionation yielded:

4,2-Ethylhexyl-1,4-dihydrodiphenyl, 25 g, b.p. 210-211° at 5 mm, solidification point -40° (glass), n_D^{20} 1.5460, d_4^{20} 0.9425, MR_D 90.09; calc. 88.92.
Found %: C 89.86, 90.00; H 10.20, 10.35. $C_{20}H_{28}$. Calculated %: C 89.46; H 10.54.

1,4-Di-2-ethylhexyl-1,4-dihydrodiphenyl, 15 g, b.p. 269-270° at 5 mm, solidification point -19° (glass), n_D^{20} 1.5200, d_4^{20} 0.9187, MR_D 125.72; calc. 125.86.
Found %: C 88.15, 88.00; H 12.10, 11.92. $C_{26}H_{44}$. Calculated %: C 88.35; H 11.60.

Reaction of 1,4-dilithium-1,4-dihydrodiphenyl with sec-octyl bromide. For the reaction were taken 77 g diphenyl, 400 ml ether, 200 ml benzene, and 7 g lithium. Shaking was carried out for 60 hours. 140 g octyl bromide was added. Yield 30 g alkylbiphenyl. Fractionation yielded:

4-Sec-octyl-1,4-dihydrodiphenyl, 22 g, b.p. 208° at 5 mm, solidification point -38° (glass), n_D^{20} 1.5500, d_4^{20} 0.9440, MR_D 90.42; calc. 88.92.
Found %: C 89.87, 90.08; H 9.96, 10.00. $C_{20}H_{28}$. Calculated %: C 89.55; H 10.45.

1,4-Di-sec-octyl-1,4-dihydrodiphenyl, 8 g, b.p. 258° at 5 mm, solidification point 18° (glass), n_D^{20} 1.5297, d_4^{20} 0.9285, MR_D 125.52; calc. 125.85.
Found %: C 88.50, 88.45; H 11.04, 11.06. $C_{28}H_{44}$. Calculated %: C 88.35; H 11.65.

Reaction of 1,4-dilithium-1,4-dihydrodiphenyl with n-nonyl bromide. For the reaction were taken 77 g diphenyl, 400 ml ether, 200 ml benzene, and 7 g lithium. Shaking was carried out for 80 hours. 105 g n-nonyl bromide was added. Yield 28 g alkylbiphenyls. Isolated:

4-n-Nonyl-1,4-dihydrodiphenyl, 18 g, b.p. 223-224° at 5 mm, m.p. 28°.
Found %: C 89.54, 89.61; H 10.52, 10.47. Calculated %: C 89.64; H 10.36.

1,4-Di-n-nonyl-1,4-dihydrodiphenyl, 10 g, b.p. 287-288° at 5 mm, solidification point - 2° (crystals), n_D^{20} 1.5190, d_4^{20} 0.9132, MR_D 135.58; calc. 135.30.
Found %: C 88.62, 88.67; H 11.44, 11.41. $C_{30}H_{48}$. Calculated %: C 88.23; H 11.77.

SUMMARY

1. It was shown that both monoalkyldihydrodiphenyls as well as dialkylhydrodiphenyls form during reactions of 1,4-dilithium-1,4-dihydrodiphenyl with alkyl halides (n-hexyl and n-nonyl bromides, sec-octyl bromide and 2-ethylhexyl bromide).

2. It was established that 1,4-di-n-alkylhydrodiphenyls, despite their great molecular weight, have a solidification point 30-40° lower than 4-alkyl-1,4-dihydrodiphenyls, due evidently to their so-called T-shaped structure.

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Received December 22, 1955

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[illegible] 1,4-dihydronaphthalene [illegible]
[illegible]
Found %: C 88.94, 88.86; H 11.04, 11.06 [illegible]

Reaction of 1,4-dihydronaphthalene [illegible]
[illegible] yield 32 g [illegible]

[illegible]
Found %: [illegible]

1,4-[illegible]
[illegible]
Found %: [illegible]

CONCLUSIONS

1. It was shown that [illegible] 1,4-dihydronaphthalene [illegible]

2. It was established that [illegible]

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Received December 22, 1959

THE ORGANOMETAL SYNTHESIS OF DIBIPHENYLALKANES AND THEIR HYDROGENATION

A. D. Petrov, E. P. Kaplan and Z. I. Letina

Up to now a very small number of this series of hydrocarbons has been synthesized: di-p-biphenylmethane [1], 1,2-di-o-biphenylethane [2], 1,2-di-p-biphenylethane [3], 1,1,-di-p-biphenylyl-2,2-dimethylpropane [4], 3,4-di-p-biphenylhexane [5]. As regards the properties of these hydrocarbons it is interesting to mention that whereas the 1,2-di-p-biphenylethane has a m. p. of 199°, its isomeric 1,2-di-o-biphenylethane is a liquid. The fatty-aromatic hydrocarbons of this series have been almost devoid of hydrogenation study, and consequently the properties of the indicated type of naphthenic hydrocarbons with composition C_nH_{2n-6} have also remained unknown. In addition, the naphthenic hydrocarbons belonging to this series very probably enter into the composition of the high-molecular fractions of natural petroleums.

In the present study we prepared a number of dibiphenylmethane homologs by reacting p-diphenyl bromide with the esters of acids (acetic, butyric, caprylic) and then hydrogenating the corresponding tertiary alcohols over copper-chromium catalyst. The dibiphenylpropylmethane and dibiphenylheptylmethane proved to be solids with m. p. 78° and 70°, respectively. However, their hydrides, obtained over active nickel catalysts, already proved to be liquids with f. p. +20 and +2°, which also permitted determining their viscosity at various temperatures. It is interesting to mention the gradual decrease in melting point (freezing point) with increase in the side-chain length (from +46° for dibicyclohexylmethylmethane to +20° for dibicyclohexylpropylmethane and +2° for dibicyclohexylheptylmethane). A similar phenomenon was also repeatedly observed earlier in various series of the so-called T-shaped hydrocarbons [6]. The hydrocarbon with a normal chain of 4 hydrogenated phenyl rings (hydrogenated quaterphenyl) had a considerably higher melting point (+135°).

EXPERIMENTAL

1. Preparation of dibicyclohexylmethane. p-Bromodiphenyl was obtained by the bromination of diphenyl with bromine in glacial acetic acid solution. It was separated from the dibromodiphenyl by distillation and recrystallization from CH_3OH.

To 24 g of magnesium in 100 ml of ether at ether boil was added in portions 250 g of p-bromodiphenyl, dissolved in 1 liter of ether. The reaction begins after 5 hours. To the Grignard reagent at room temperature was added 40 g of ethyl acetate, and when all of this was added the stirring under heating was continued for another 12 hours. The decomposition was effected with 10% CH_3COOH. The ether portion of the solution was separated, and the ether-insoluble quaterphenyl was filtered. After distilling off the ether the mass crystallized. Repeated recrystallization from isooctane gave 70 g of dibiphenylethylene with m. p. 205°. Literature: m. p. 211° [5], 204° [3].

The dibiphenylethylene was hydrogenated in an autoclave. The charge was 70 g of dibiphenylethylene, 200 ml of dimethylcyclohexane and 5 g of Raney Ni catalyst. The initial hydrogen pressure was 110 atm., and the hydrogenation was run at 210°. Removal of the solvent by distillation gave 63 g of dibicyclohexylmethylmethane.

B. p. 218-220° at 5 mm, m. p. 46°.

Found %: C 87.46, 87.56; H 12.59, 12.60. $C_{26}H_{46}$. Calculated %: C 87.15; H 12.85.

2. Preparation of dibicyclohexylpropylmethane. Dibiphenylpropylcarbinol was prepared from 24 g of Mg and 233 g of the diphenyl bromide in 1 liter of ether under conditions similar to those used to synthesize the dibiphenylethylene. Recrystallization from petroleum ether gave 80 g of the alcohol with m. p. 132°.

Found %: C 88.97; H 6.90. $C_{28}H_{26}O$. Calculated %: C 88.18; H 7.63.

Reduction of the alcohol group. Into an autoclave was charged 51 g of the alcohol, 250 ml of xylene and 10 g of copper-chromium catalyst. The initial hydrogen pressure was 120 atm., and the hydrogenation temperature was 240-250°. We obtained 45 g of the dibiphenylpropylmethane, which after recrystallization from isooctane had m. p. 78°.

Found %: C 92.24, 92.20; H 7.00, 7.00. $C_{28}H_{26}$. Calculated %: C 92.81; H 7.18

Hydrogenation of the aromatic rings. Into an autoclave was charged 25 g of the hydrocarbon, 170 ml of dimethylcyclohexane and 3 g of Raney nickel. The initial pressure was 110 atm., and the hydrogenation temperature was 200°. We obtained 22 g of the dibicyclohexylpropylmethane.

B. p. 233-235° at 5 mm, f. p. 20° (glass), d_4^{50} 0.9293, d_4^{20} 0.9475, $\nu_{50} =$ 21.4789 centistokes, $\nu_{100} =$ 0.4998 centistokes.

Found %: C 87.20, 87.35; H 12.60, 12.75. $C_{28}H_{50}$. Calculated %: C 86.96; H 13.03.

3. Preparation of dibicyclohexylheptylmethane. Dibiphenylheptylcarbinol was obtained from 24 g of Mg, 250 g of the biphenyl bromide and 81 g of ethyl caprylate in 800 ml of ether. Recrystallization from petroleum ether gave 60 g of the alcohol with m. p. 115°.

Found %: C 87.91, 88.09; H 8.11, 7.95. $C_{32}H_{34}O$. Calculated %: C 88.42; H 7.88.

Reduction of the alcohol group. The charge was 30 g of the alcohol, 200 ml of xylene and 5 g of copper-chromium catalyst. The initial pressure was 95 atm., and the temperature was 240-250°. Recrystallization from isooctane gave 28 g of the hydrocarbon with m. p. 70°.

Found %: C 91.78, 91.88; H 8.20, 8.17. $C_{32}H_{34}$. Calculated %: C 91.86; H 8.13.

Hydrogenation of the aromatic rings. The charge was 28 g of the hydrocarbon, 150 ml of dimethylcyclohexane and 4 g of Raney Ni. The initial pressure was 100 atm., and the hydrogenation temperature was 200°. After hydrogenation the bicyclohexylheptylmethane was obtained as a clear limpid oil.

B. p. 280-282° at 5 mm, f. p. 2° (glass), d_4^{50} 0.9131, d_4^{20} 0.9317, $\nu_{50} =$ 7.538 centistokes, $\nu_{100} =$ 0.3621 centistokes.

Found %: C 87.00, 87.10; H 13.20, 13.12. $C_{32}H_{56}$. Calculated %: C 86.85; H 13.12.

Hydrogenation of quaterphenyl. The charge was 72 g of quaterphenyl, 190 ml of dimethylcyclohexane and 10 g of Raney Ni. The initial pressure was 120 atm., and the hydrogenation temperature was 290°. The obtained product had m. p. 135°.

Found %: C 87.03; H 12.89. $C_{24}H_{42}$. Calculated %: C 87.27; H 12.73.

SUMMARY

1. The hydrogenated quaterphenyl, dibicyclohexylmethylpropyl- and heptylmethanes, and dibiphenylpropyl- and heptylmethanes were synthesized for the first time. We determined the viscosity of the liquid naphthenic hydrocarbons at various temperatures.

2. It was shown that in the dicyclohexylalkylmethane series the freezing points decrease with increase in the length of the alkyl chain.

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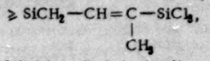
Received December 22, 1955.

Institute of Organic Chemistry,
Academy of Sciences of the USSR

DIRECT SYNTHESIS OF ALKYLPOLYSILANE CHLORIDES

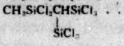
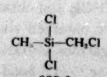
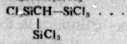
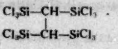
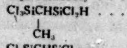
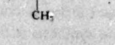
A. D. Petrov, S. I. Sadykhzade, E. A. Chernyshev and V. F. Mironov

One of the most promising methods for the synthesis of alkylsilane chlorides is the direct method. Together with alkylmonosilane chlorides, it also permits synthesizing alkyldisilane and polysilane chlorides, the preparation of which by some other method is in general almost incapable of realization, at least at the present time. For the purpose of synthesizing disilane chlorides by the direct method we used methylene chloride [1, 2] and dichloroethane [1], where together with the disilane chlorides $Cl_3Si(CH_2)_nSiCl_3$ we also isolated heterocyclic polysilane chlorides with silicon atoms in the ring. We also used CH_3CHCl_2, $ClCH_2CHClCH_3$ and $Cl(CH_2)_4Cl$ [3] in the direct synthesis method, but here we obtained only very small yields of reaction products. Two of us [4] repeated the direct synthesis with CH_3CHCl_2 and obtained completely different results, both qualitatively and quantitatively, and specifically, we obtained vinyltrichlorosilane in 26% yield. It should be mentioned that in all of the enumerated investigations we failed to isolate any intermediate products that could have served as possible evidence that only one C−Cl bond had reacted. Recently two of us [5] had shown that the use of 1,3-dichloro-2-butene, showing unequal reactivity of the chlorine atoms, already permitted us, depending on the temperature conditions of the reaction, to obtain both the monosilane and disilane chlorides $\geqslant SiCH_2CH{=}CClCH_3$ and  $\geqslant SiCH_2{-}CH{=}\underset{CH_3}{C}{-}SiCl_3$. This almost exhausts the material existing in the literature on the utilization of dichloroalkyls in the direct synthesis method. As regards data on the involvement of tri- and tetra- chlorides in the synthesis, then here they are limited to a study of $CHCl_3$ [3] and CCl_4 [6], where in both cases alkylsilane chlorides failed to be obtained.

The purpose of our study, which was recently published as a preliminary communication [7], was to investigate the possibility of obtaining alkylsilane chlorides with three and more silicon atoms by the direct method. Together with this, as a purely synthetic problem, we wanted to obtain a clearer picture of the direct synthesis process with the utilization of CH_2Cl_2, $ClCH_2CH_2Cl$, $CHCl_3$ and CCl_4, and consequently as reaction components we gave preferential choice to those chloro- or dichloroalkylsilane chlorides, already having either one or two silicon atoms in the molecule, that could formally appear as intermediate products in the direct synthesis with the above-indicated dichlorides, chloroform and carbon tetrachloride.

Chloromethyltrichlorosilane Cl_3SiCH_2Cl, in its structure being a formal intermediate product of the direct synthesis with methylene chloride at 340-370°, readily reacted with a copper-silicon mass (80% Si-20% Cu) and the desired bis(trichlorosilyl)-methane was obtained in 30% yield, based on the condensate. In addition, we also isolated from the condensate a product (yield 8.5%) containing three silicon atoms (VI) (see Table 2). Together with the formation of these two substances there also proceeded quite intense reduction of the starting chloride with the formation of methyltrichlorosilane (10%). A considerable portion (30%) of the original chloride was recovered unchanged. Incidentally, in the synthesis with CH_2Cl_2 this chloride was not isolated [7]. These results suggest that the direct synthesis with CH_2Cl_2 probably proceeds, not through the formation of Cl_3SiCH_2Cl, but by a different mechanism. $CH_3SiCl_2CH_2Cl$ also showed approximately similar behavior in the reaction, where the alkylsilane chloride (28.7%) and alkyltrisilane chloride (16.7%) were also obtained, and the starting chloride was recovered unchanged, although in smaller amount (17.3%). In view of the higher hydrogen content in the starting molecule there was even more intense reduction to $(CH_3)_2SiCl_2$ (21.0%) in the direct synthesis.

TABLE 1

Starting substance	Composition of crude mixture (condensate)	Boiling point	Amount in crude mixture (in %)
Cl_3SiCH_2Cl	$SiCl_4$	55—56°	2.0
200 *	CH_3SiCl_3	64—66	10.0
198 **	Cl_3SiCH_2Cl	115—117	30.0
300—370° ***	$Cl_3SiCH_2SiCl_3$	180.5—181	30.0
	$(Cl_3SiCH_2)_2SiCl_2$	157—158 (6 mm)	8.5
$Cl_3SiCH_2CH_2Cl$	$SiCl_4$	55—56°	3.0
300 *	$Cl_3SiC_2H_5$	97—98	8.3
290 **	$Cl_3SiCH{=}CH_2$	90—92	5.0
360—370° ***	$Cl_3SiCH_2CH_2SiCl_2$	183—184	3.3
	$Cl_3SiCH_2CH_2SiCl_3$	199—199.2	43.6
	$(Cl_3SiCH_2CH_2)_2SiCl_2$	154.5—156 (4.5mm)	10.0
$CH_3SiCl_2CHCl_2$	$SiCl_4$	55—56°	4.9
300 *	Cl_3SiCH_3	64—66	25.6
285 **	$CH_3SiCl_2CH_2Cl$	120—122	4.2
360—370° ***	$CH_3SiCl_2CH_2SiCl_3$	182.5—183	10.5
	 $CH_3SiCl_2\underset{\substack{\vert\\SiCl_3}}{CH}SiCl_3$	124—125 (10mm) M. p. 49—50°	14.0
 $CH_3-\underset{\substack{\vert\\Cl}}{\overset{\substack{Cl\\\vert}}{Si}}-CH_2Cl$	$SiCl_4$	55—56°	2.0
300 *	$(CH_3)_2SiCl_2$	70—70.5	21.0
297 **	$CH_3SiCl_2CH_2Cl$	120—122	17.3
360—370° ***	$CH_3SiCl_2CH_2SiCl_3$	183.5—184.5	28.7
	$(CH_3SiCl_2CH_2)_2SiCl_2$	123—124 (3mm)	16.7
$Cl_3SiCHClSiCl_3$	$SiCl_4$	55—56°	6.3
260 *	$Cl_3SiCH_2SiCl_3$	179.9	16.7
240 **	 $Cl_3Si\underset{\substack{\vert\\SiCl_3}}{CH}-SiCl_3$	108—109 (3mm) M. p. 57°	29.8
360—370° ***	 $\begin{array}{l}Cl_3Si-CH-SiCl_3\\ \qquad\ \ \vert\\ Cl_3Si-CH-SiCl_3\end{array}$	139—140 (3mm)	10.4
	—	—	—
$Cl_3SiCH_2CHCl_2$	$HSiCl_3$	31—33°	3.2
180 *	$SiCl_4$	54—56	13.0
155 **	$Cl_3SiCH{=}CH_2$	90—93	15.2
360—370° ***	$Cl_3SiCH{=}CHCl$	132—132.5	9.1
	—	—	—
$Cl_3SiCHClCH_3$	$SiCl_4$	55—56°	3.3
600 *	$Cl_3SiC_2H_5$	97—98	28.3
592 **	$Cl_3SiCH{=}CH_2$	89—91	
360—370° ***	$Cl_3SiCHClCH_3$	136—138	5.0
	 $Cl_3Si\underset{\substack{\vert\\CH_3}}{CH}SiCl_2H$	180.4—181	5.0
	 $Cl_3Si\underset{\substack{\vert\\CH_3}}{CH}SiCl_3$	197—197.3	25.0

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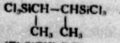
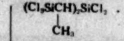
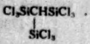
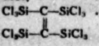
* Amount of substance taken for reaction in grams.

** Amount of crude mixture (condensate) obtained in grams.

*** Furnace temperature during reaction.

TABLE 1 (Continued)

Starting substance	Composition of crude mixture (condensate)	Boiling point	Amount in crude mixture (in %)
	 $Cl_3SiCH(CH_3)-CH(CH_3)SiCl_3$	237–239	8.3
	 $(Cl_3SiCH(CH_3))_2SiCl_2$	227–5–275	6.6
$Cl_3SiCHCl_2$ 270 * 255 ** 360–370° ***	$SiCl_4$	55–56°	35.2
	Cl_3SiCH_3	66–66.5	3.5
	Cl_3SiCH_2Cl	117–117.5	3.5
	$Cl_3SiCH_2SiCl_3$	58–59 (8mm)	22.4
	 $Cl_3SiCH(SiCl_3)SiCl_3$	113–114.5 (4mm) M. p. 55–56	13.0
$Cl_3SiCCl_2SiCl_3$ 240 * 220 ** 360–370° ***	$SiCl_4$	55–56°	18.2
	 $(Cl_3Si)_2C=C(SiCl_3)_2$	206–208 (12mm) M. p. 55–59°	11.4

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* Amount of substance taken for reaction in grams.

** Amount of crude mixture (condensate) obtained in grams.

*** Furnace temperature during reaction.

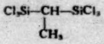
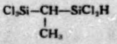
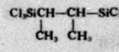
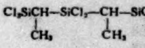
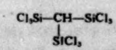
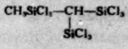
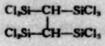
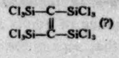
The α- and β-chloroethyltrichlorosilanes also entered into the reaction with good yields. The sum of the reaction products of α-chloroethyltrichlorosilane with silicon was, the same as in the previous cases, about 40%, but here the amount of starting chloride recovered from the reaction dropped to 5%. Together with reduction of the chloride, here there also proceeded HCl cleavage with the formation of vinyltrichlorosilane. β-Chloroethyltrichlorosilane showed more complete reactivity. Here the amount of reaction products with silicon approximated 60%. In view of the higher reactivity shown in this case by the C−Cl bond we already failed to isolate any of the starting chloride, while the amount of reduction and HCl-cleavage products showed more than a two-fold decrease when compared with the α-isomer. The absence of ethyl- and vinyltrichlorosilanes in the reaction products of 1,2-dichloroethane with silicon indicates that also in the case of this dichloroethane the direct synthesis probably proceeds, not through the intermediate formation of $Cl_3SiCH_2CH_2Cl$, but by a different mechanism.

Very interesting results were obtained when $Cl_3SiCHCl_2$ was used in the reaction. As can be seen from the formula, this compound could appear as an intermediate product of the direct synthesis with $CHCl_3$. However, as we had already mentioned, alkylsilane chlorides failed to be formed in the direct synthesis with chloroform. It was not clear whether the reaction would proceed in our case. It was found that the reaction does go, but, as was to be expected, with considerable cleavage of the $CHCl_2$ group and the formation of $SiCl_4$. As the result of carbonization and hydrogen evolution there also proceeded reduction of the starting chloride to CH_3SiCl_3 and Cl_3SiCH_2Cl and the formation of $Cl_3SiCH_2SiCl_3$ (22.4%) from the latter. Tris-(trichlorosilyl)-methane (IX) (Table 2) was formed here in 13% yield.

The second intermediate product, which could be formed in the direct synthesis with $CHCl_3$, is $Cl_3SiCHClSiCl_3$ and its behavior in the direct synthesis was studied by us. It was revealed that in this case cleavage at the Si−C bond already proceeds to a lesser degree; there is partial reduction of the starting chloride to $Cl_3SiCH_2SiCl_3$ (16.7%), and the tris-(trichlorosilyl)-methane is formed in good yield (29.1%).

Only $Cl_3SiSiCl_3$ [3] was isolated by the Canadian investigators in the direct synthesis with $CHCl_3$. The absence of hexachlorodisilane in our case and the obtaining of a number of other products indicates that the direct synthesis with $CHCl_3$ proceeds, not through the formation of $Cl_3SiCHCl_2$ and $Cl_3SiCHClSiCl_3$, but by a different mechanism.

TABLE 2

No.	Substance formula	Name	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}
(I)	 $\underset{CH_3}{Cl_3Si{-}\overset{}{C}H{-}SiCl_3}$	1,1-Bis-(trichlorosilyl)-ethane	197—197.3° (730)	1.4842	1.5121
(II)	 $Cl_3Si{-}\underset{CH_3}{CH}{-}SiCl_2H$	1-Trichlorosilyl-1-dichlorosilylethane	180.4—181° (730)	1.4780	1.4373
(III)	$CH_3SiCl_2CH_2SiCl_3$	Methyl-methyltrichlorosilyl-dichlorosilane	183.5—184.5° (746)	1.4692	1.4107
(IV)	 $Cl_3Si\underset{CH_3}{CH}{-}\underset{CH_3}{CH}{-}SiCl_3$	2,3-Bistrichlorosilylbutane	237—239° (736)	1.4910	1.4332
(V)	 $Cl_3Si\underset{CH_3}{CH}{-}SiCl_2{-}\underset{CH_3}{CH}{-}SiCl_3$	1,1,1,3,3,5,5,5- Octachloro-2,4-dimethyl-1,3,5-trisilpentane	272.5—275° (736)	1.4990	1.4736
(VI)	$Cl_3SiCH_2{-}SiCl_2{-}CH_2SiCl_3$	1,1,1,3,3,5,5,5- Octachloro-1,3,5-trisilpentane	157—158° (6)	1.4970	1.5423
(VII)	$CH_3SiCl_2CH_2SiCl_2CH_2SiCl_2CH_3$	2,2,4,4,6,6- Hexachloro-2,4,6-trisilheptane	123—124° (3)	1.4905	1.3782
(VIII)	$Cl_3SiCH_2CH_2SiCl_2CH_2CH_2SiCl_3$	1,1,1,4,4,7,7,7- Octachloro-1,4,7-trisilheptane	154.5—156° (4.5) M.p. 44—46°	—	—
(IX)	 $Cl_3Si{-}\underset{SiCl_3}{CH}{-}SiCl_3$	Tris-(trichlorosilyl)-methane	108—109° (3) M.p. 57°	—	—
(X)	 $CH_3SiCl_2{-}\underset{SiCl_3}{CH}{-}SiCl_3$	Methyldichlorosilyl-bis-(trichlorosilyl)-methane	124—125°(10) M.p. 49—50°	—	—
(XI)	 $\begin{array}{c}Cl_3Si{-}CH{-}SiCl_3\\ \vert\\ Cl_3Si{-}CH{-}SiCl_3\end{array}$	1,1,2,2- Tetra-(trichlorosilyl)-ethane	139—140° (3)	1.5212	1.6929
(XII)	 $\begin{array}{c}Cl_3Si{-}C{-}SiCl_3\\ \Vert\\ Cl_3Si{-}C{-}SiCl_3\end{array}$ (?)	Tetratrichlorosilyl-ethylene	206—208°(15) M.p. 55—59°	—	—

We also studied in the direct synthesis the possible intermediate product of the second step of the direct synthesis with CCl_4, namely $Cl_3SiCCl_2SiCl_3$. It was revealed that here also there is considerable cleavage of the Si–C bond to the starting polychloride. In this reaction we were able to isolate, other than $SiCl_4$, only a small amount of crystalline product with m. p. 55-59°, the structure of which we were unable to establish, but based on the elementary analysis of the possible products it comes closest to Formula (XII) (Table 2).

We isolated tetrachloroethylene [6] in the direct synthesis with CCl_4. The absence of this substance in the condensate in our case and the obtaining of other products indicates that also with CCl_4 the direct synthesis proceeds, not through the formation of $Cl_3SiCCl_2SiCl_3$, but by a different mechanism.

Considerable decomposition of the starting polychloride was also observed in the reaction with $CH_3SiCl_2CHCl_2$. Here the decomposition product was Cl_3SiCH_3 (25.6%). The same as in the reaction with $Cl_3SiCHCl_2$, here the starting polychloride was reduced to $CH_3SiCl_2CH_2Cl$ and the latter was transformed by reaction with silicon to $CH_3SiCl_2CH_2SiCl_3$. (Methyldichlorosilyl)-bis-(trichlorosilyl)-methane (X) was also isolated (in 14% yield). When β, β-dichloroethyltrichlorosilane was used in the direct synthesis we were unable to isolate any alkyldi- and alkyltrisilane chlorides in the pure form. As in the previous cases, here there occurred decomposition at the Si–C bond, and also the cleavage of HCl with the formation of $Cl_3SiCH{=}CHCl$ and reduction of the latter to

MR_D		Found (%)				Empirical formula	Calculated (in %)			
found	calculated	C	H	Si	Cl		C	H	Si	Cl.
56.22	56.21	8.34, 8.35	1.49, 1.42	19.11, 19.47	71.01, 71.05	$C_2H_4Si_2Cl_6$	8.08	1.34	18.86	71.74
51.71	52.21	9.34, 9.31	1.69, 1.67	21.34, 21.19	67.94, 68.21	$C_2H_5Si_2Cl_5$	9.14	1.90	21.33	67.61
51.84	51.95	9.81, 9.74	2.12, 2.14	21.34, 21.04	66.32, 66.15	$C_2H_5Si_2Cl_5$	9.14	1.90	21.33	67.60
65.68	65.47	15.10, 14.91	2.38, 2.29	17.41, 17.34	65.62, 65.12	$C_4H_8Si_2Cl_6$	14.77	2.46	17.23	65.39
84.25	83.62	12.60, 12.56	1.85, 1.65	19.62, 19.22	66.13, 66.35	$C_4H_8SiCl_8$	11.32	1.89	19.81	66.98
75.15	74.36	—	—	21.77, 21.92	—	$C_2H_4SiCl_8$	—	—	21.23	—
74.54	75.10	14.34, 14.28	2.79, 2.80	23.61, 23.46	59.46, 58.64	$C_4H_{10}SiCl_6$	13.56	2.84	23.69	59.90
—	—	12.12, 12.01	1.94, 2.04	19.30, 19.57	65.66, 65.78	$C_4H_8Si_3Cl_8$	11.32	1.89	19.81	66.98
—	—	3.09, 3.25	—	20.68, 20.87	74.94, 75.40	$CHSi_3Cl_9$	2.90	0.21	20.22	76.68
—	—	7.36, 7.33	1.11, 1.13	20.91, 21.20	69.66, 69.47	$C_2H_4Si_3Cl_8$	6.06	1.01	21.20	71.71
—	—	4.55, 4.53	0.32, 0.37	18.83, 20.64	73.49, 72.76	$C_2H_2Si_4Cl_{12}$	4.26	0.35	19.86	75.53
—	—	4.63, 4.59	—	22.02, 22.11	72.99, 72.97	$C_2Si_4Cl_{12}$	4.27	—	19.93	76.00

$Cl_3SiCH=CH_2$. Without question there was also reduction to $Cl_3SiCH_2CH_2Cl$, but in view of its higher reactivity this chloride evidently showed immediate reaction with silicon. In this way the absence of $Cl_3SiC_2H_5$ in the reaction products is explained. A considerable portion of the high-boiling products represented a very complex mixture, and we found it impossible to isolate any individual substances by distillation.

As a result, in the direct synthesis using mono- and dichloroalkylsilane chlorides there occurs not only their reaction with silicon, but also cleavage of the starting chlorides at the Si–C bond, pyrolysis with hydrogen evolution, reduction of the chlorides by hydrogen, and in individual cases, condensation of the chlorides. The cleavage proceeds more easily the greater the number of chlorine atoms in the alkyl radical of the starting polychloride. The amount of reduced products increases with increase in the hydrogen content of the starting polychloride. These processes can show considerable reduction in the case of chlorides with a highly reactive C–Cl bond (for example, $Cl_3SiCH_2CH_2Cl$).

The reaction was run in a catalyst-filled glass tube contained in an electric furnace, the tube having a length of 60.0 cm and a diameter of 4.0 cm, filled with pieces (5-10 mm) of Si–Cu alloy (80 : 20), and with an average passage rate for the starting substance of 20.0-25.0 ml/hr. A 35-theoretical plate column was used to distill the obtained condensate. The reaction temperature, amounts of starting substances and condensate, and also the distillation results, are given in Table 1. The constants and analyses of the substances obtained for the first time are given in Table 2. The starting mono- and dichloroalkylsilane chlorides were prepared by the chlorination of CH_3SiCl_3, $(CH_3)_2SiCl_2$, $C_2H_5SiCl_3$, $Cl_3SiCH_2SiCl_3$, $ClCH_2CH_2SiCl_3$ and $CH_3CHClSiCl_3$ under the conditions described earlier [8].

SUMMARY

1. In principle the possibility was shown of directly synthesizing alkylpolysilane chlorides with three and four silicon atoms from chlorinated alkylsilane and -disilane chlorides.

2. It was shown in the direct synthesis with mono- and polyalkylsilane chlorides that, together with their reaction with silicon, there also occurs cleavage of the Si—C bond and pyrolysis with hydrogen evolution and reduction of the starting polychlorides by the latter, in individual cases with great intensity.

3. It was postulated that the direct synthesis with CH_2Cl_2, $ClCH_2CH_2Cl$, $CHCl_3$ and CCl_4 proceeds, not through the formation of intermediate products with reaction of only one C—Cl bond at the start, but by a different mechanism.

4. We obtained for the first time 12 new alkylpolysilane chlorides with two, three and four silicon atoms.

LITERATURE CITED

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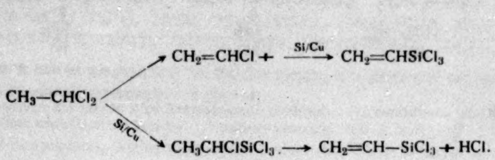
Received December 26, 1955.

Institute of Organic Chemistry,
Academy of Sciences of the USSR

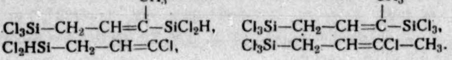
DIRECT SYNTHESIS OF SILANE CHLORIDES FROM DICHLORIDES OF THE VINYLALLYL TYPE

A. D. Petrov, S. I. Sadykhzade, N. P. Smetankina and Yu. P. Egorov

As is known, saturated dichlorides with the halogens attached to different carbon atoms (of the $Cl-(CH_2)_x-Cl$ type) react with Si/Cu only under simultaneous reaction of both chlorine atoms, which leads to the formation of hexachlorodisilanes [1, 2] of the $Cl_3Si-(CH_2)_x-SiCl_3$ type. In contrast to methylene chloride, its closest homologs CH_3CHCl_2 and $CH_3CCl_2CH_3$, as was shown [3], form, in addition to the corresponding hexachlorodisilanes, also unsaturated monosilane chlorides. The latter are obtained in higher yields than in the case of their direct synthesis from vinyl halides, which suggests that either higher yields of silane chlorides are obtained when the vinyl chlorides are utilized at the moment of their formation, or that intermediate saturated chloro-substituted monosilanes are formed, which then cleave HCl:

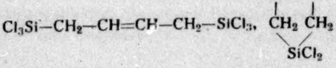


The formation of a product from the reaction of a dichloride with Si/Cu in which only one chlorine atom had reacted was first observed on the example of the unsaturated dichloride 1,3-dichloro-2-butene [4]. When the synthesis was run at a somewhat lower temperature, there were obtained from this halide, together with disilane chlorides, also chloro-substituted monosilane chlorides:



$$Cl_3Si-CH_2-CH=C(CH_3)-SiCl_2H,\quad Cl_3Si-CH_2-CH=C(CH_3)-SiCl_3,$$
$$Cl_2HSi-CH_2-CH=CCl,\quad Cl_3Si-CH_2-CH=CCl-CH_3.$$

1,4-Dichloro-2-butene, as was shown [5], together with the corresponding disilane chloride, also forms a cyclic monosilane chloride. This is the first cyclic silicon compound to be obtained under the direct synthesis conditions:



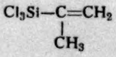
$$Cl_3Si-CH_2-CH=CH-CH_2-SiCl_3,$$

A study of the behavior of the lower homologs of the above-indicated dichlorobutenes in the direct synthesis reaction, and specifically of 1,3-dichloro-1-propene and 2,3-dichloro-1-propene, was the subject of the present investigation. In contrast to 1,3-dichloro-2-butene, its next lower analog, 1,3-dichloro-1-propene, failed to react with Si/Cu at 270-280°. The reaction went when the temperature was raised to 380°, but here instead of obtaining the disilane chloride, as we had hoped, a mixture of monosilane chlorides – allyltrichlorosilane (I) and propenyltrichlorosilane (II) – was formed:

$$\underset{(I)}{Cl_3Si-CH_2-CH{=}CH_2} \qquad \underset{(II)}{Cl_3Si-CH{=}CH-CH_3},$$

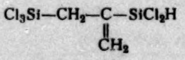
being the result of replacement of both the vinyl and allyl hydrogens by chlorine atoms. (Incidentally, it is possible that only the allyl chlorine atom reacted with Si/Cu, while the vinyl chlorine atom was replaced by hydrogen, and then the formation of (II) is explained by the partial isomerization of allyltrichlorosilane.)

In comparison to 1,3-dichloro-1-propene, 2,3-dichloro-1-propene reacted with Si/Cu at a lower temperature (275-290°) and by a different scheme. Here, together with the two monosilane chlorides – allyltrichlorosilane (I) and isopropenyltrichlorosilane (III) (the formation of which suggests both reaction with Si and corresponding replacement by hydrogen of both the allyl and vinyl chlorine atoms), the reaction mixture also contained the two disilane chlorides: 2-dichlorosilyl-3-trichlorosilyl-1-propene (IV) and 2,3-ditrichlorosilyl-1-propene (V):



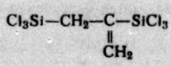
$Cl_3Si-C(CH_3){=}CH_2$

(III)



$Cl_3Si-CH_2-C({=}CH_2)-SiCl_2H$

(IV)



$Cl_3Si-CH_2-C({=}CH_2)-SiCl_3$

(V)

As a result, it is evident that α-chloroallyl chloride is characterized by a higher reactivity than is β-chloroallyl chloride.

EXPERIMENTAL

1,3-Dichloro-1-propene with b. p. 106.5-107° was obtained in an amount of about 600 g from glycerol α, γ-dichlorohydrin under the conditions of [6]. 2,3-Dichloro-1-propene with b. p. 92.3°, d_4^{20} 1.2095, n_D^{20} 1.4599, was obtained from glycerol trichlorohydrin under the conditions of [7].

1. Five hundred grams of 1,3-dichloro-1-propene was passed at a rate of 25 g/hr. through a (80:20) Si/Cu alloy heated to 370-380°. We obtained 380 g of condensate, the fractionation of which gave the following fractions: 1st, b. p. 31°, 16 g ($HSiCl_3$); 2nd, 32-55°, 7 g; 3rd, 55-56°, 56 g ($SiCl_4$); 4th, 57-58°, 4 g; 5th, 78-80°, 10 g; 6th, 80-112°, 37 g; 7th, 112-117°, 65 g; 8th, 117-122°, 7 g; 9th, 122-126°, 48 g. The residue and losses from the distillation totalled 130 g. The 7th fraction was allyltrichlorosilane (I) and after redistillation had the following constants:

B. p. 114.5-115° at 743 mm, d_4^{20} 1.2011, n_D^{20} 1.4460, MR_D 38.96; calc. 38.96.

From [8], b. p. 116-118°, d_4^{25} 1.2150, n_D^{20} 1.4449.

The substance was methylated. Here we obtained trimethylallylsilane:

B. p. 83.3° at 752 mm, n_D^{20} 1.4068, d_4^{20} 0.7188, MR_D 39.11; calc. 39.07.

Raman spectrum in (cm^{-1}): 414(0), 556(5), 627(3), 699(2b), 990(0), 1156(3), 1192(2), 1300(3), 1390(1), 1420(2), 1630(5).

The following constants are given in the literature [9] for trimethylallylsilane: b. p. 84.9°, n_D^{20} 1.4074, d_4^{20} 0.7193, and also an identical characterization of the spectrum [10].

The 9th fraction after redistillation through a column was propenyltrichlorosilane (II):

B. p. 124-126° at 747 mm, d_4^{20} 1.2154, n_D^{20} 1.4490, MR_D 38.73; calc. 38.96.

From [11], b. p. 126.5°, d_4^{25} 1.2140, n_D^{20} 1.4513.

This substance was also methylated. The obtained trimethylpropenylsilane had the following constants:

B. p. 86.2-86.5° at 757 mm, n_D^{20} 1.4065, d_4^{20} 0.7162.

Found %: C 62.86, 62.98; H 12.31, 12.50; Si 24.77, 24.66. $C_6H_{14}Si$. Calculated %: C 63.08; H 12.37; Si 24.54.

The spectrum given below also agreed well with the spectrum of trimethylpropenylsilane [12] (in cm^{-1}): 310(1), 395(5), 498(1), 556(1), 615(8), 690(3), 706(3), 834(1), 1033(1 b), 1259(3 b), 1312(5), 1374(4 b), 1415(3 b), 1444(4), 1625(5), 1630(0).

2. 2,3-Dichloro-1-propene (900 g) was passed at a rate of 39 g/hr. through the Si/Cu alloy heated to 275-290°. Here we obtained 800 g of condensate, which after distillation through a column, gave the following fractions: 1st, b. p. 30-60°, 120 g; 2nd, 91-92°, 100 g; 3rd, 107-115°, 70 g; 4th, 148-152°, 128 g; 5th, 196-198°, 49 g; 6th, 210-212°, 70 g. The residue and losses totalled 260 g.

The 3rd fraction after redistillation through a column had the following constants: b. p. 113-115°, d_4^{20} 1.2182, n_D^{20} 1.4435.

After methylation the substance had the following constants:

B. p. 82-83.5° at 746 mm, d_4^{20} 0.7191, n_D^{20} 1.4062.

Raman spectrum (in cm^{-1}): 212(4), 240(4), 371(2), 412(1), 556(4), 573(8), 631(4), 655(4), 695(4 b), 861(1 b), 936(3), 988(1), 1154(3), 1190(2), 1250(1), 1299(4), 1395(2), 1415(5), 1444(1), 1605(3), 1630(5).

From this spectrum it can be assumed that the fraction consists of a mixture of the two silicohydrocarbons: trimethylallylsilane and trimethylisopropenylsilane [10, 12].

The 4th fraction after redistillation had the following constants: d_4^{20} 1.2824, n_D^{20} 1.4721, and apparently represented a mixture of two products. Methylation of this fraction enabled us to isolate a small amount of substance with the following constants:

B. p. 128.8° at 743 mm, $n_D^{21.8}$ 1.4391, $d_4^{21.8}$ 0.8909, MR_D 43.91; calc. 43.91.

Found %: C 48.78, 49.01; H 8.71, 8.72; Si 18.13, 18.30; Cl 23.60, 23.61. $C_6H_{13}SiCl$.
Calculated %: C 48.53; H 8.81; Si 18.89; Cl 23.84.

The Raman spectrum showed the following frequencies (in cm^{-1}): 172(6), 192(6), 237(6), 365(1), 400(3), 435(0), 498(10), 605(10), 630(0), 704(5 b), 772(1), 845(1), 860(2), 940(0), 1005(0), 1020(1), 1089(3), 1169(4), 1203(2 b). 1259(2 b), 1393(3 b), 1420(5 b), 1627(10), 2842(1), 2900(8), 2960(8), 3005(1), 3049(1), 3110(3).

Based on its spectral analysis,[*] the obtained substance can be assigned the structure of β-chloroallyltrimethylsilane $(CH_3)_3Si-CH_2-CCl=CH_2$ (VI).

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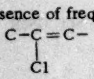
[*] 1) The presence of frequencies 3005, 3049 and 3110 cm^{-1}, almost identical with the position of analogous frequencies in



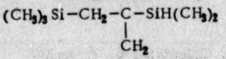
$C-C(Cl)=C-$ (3016, 3049, 3114 cm^{-1}), indicates the end position of the C=C bond and the proximity of the Cl, since usually (without chlorine) these frequencies are below 3000 and 3080 cm^{-1}.
2) The close proximity of the $-C=C-$ bond frequency (1627 cm^{-1}) and the frequency observed in allylsilanes (1630 cm^{-1}).

The 5th fraction after redistillation had the following constants:

B. p. 197° at 745 mm, n_D^{20} 1.4846, d_4^{20} 1.3901, MR_D 56.56; calc. 56.37.

Found %: C 14.84, 14.68; H 2.00, 2.22; Si 20.03, 20.33; Cl 62.68, 62.93. $C_3H_5Si_2Cl_5$. Calculated %: C 13.11; H 1.82; Si 20.40; Cl 64.66.

The fraction was subjected to methylation, after which the obtained product of structure



$(CH_3)_3Si-CH_2-\underset{\displaystyle CH_2}{\underset{|}{C}}-SiH(CH_3)_2$ had the following constants:

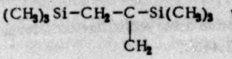
B. p. 157° at 760 mm, n_D^{20} 1.4369, d_4^{20} 0.7829.

Found %: C 56.14, 56.14; H 11.65, 11.73. $C_8H_{20}Si_2$. Calculated %: C 55.81; H 11.62.

The 6th fraction after redistillation had the following constants:

B. p. 211.2° at 745 mm, n_D^{20} 1.4971, d_4^{20} 1.4659, MR_D 60.63; calc. 60.37.

Found %: C 13.04, 12.79; H 1.45, 1.52; Si 17.91, 17.91; Cl 67.78, 68.23. $C_3H_4Si_2Cl_6$. Calculated %: C 11.69; H 1.29; Si 18.12; Cl 68.93.

Methylation of the fraction gave a product of structure  $(CH_3)_3Si-CH_2-\underset{\displaystyle CH_2}{\underset{|}{C}}-Si(CH_3)_3$ with the following constants:

B. p. 166.8° at 749 mm, n_D^{20} 1.4331, d_4^{20} 0.7929.

Found %: C 57.04, 56.76; H 11.53, 11.51; Si 29.95, 29.82. $C_9H_{22}Si_2$. Calculated %: C 57.97; H 11.89; Si 30.13.

SUMMARY

1. It was shown that 1,3-dichloro-1-propene enters into the direct synthesis reaction only at 370°, in this connection forming a mixture of monosilane chlorides: allyltrichlorosilane (I) and propenyltrichlorosilane (II).

2. 2,3-Dichloro-1-propene enters into the direct synthesis reaction even at 270°, and also at this low temperature a mixture of monosilane chlorides – allyltrichlorosilane (I) and isopropenyltrichlorosilane (III) – and disilane chlorides – 2-dichlorosilyl-3-trichlorosilyl-1-propene (IV) and 2,3-ditrichlorosilyl-1-propene (V) – is formed.

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Received December 28, 1955.

Institute of Organic Chemistry,
Academy of Sciences of the USSR

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STUDY OF SODIUM TANTALATE HYDRATES

Vikt. I. Spitsyn and N. N. Shavrova

A compound, usually assigned the composition $8Na_2O \cdot 6Ta_2O_5 \cdot 25H_2O$ [1,2] (8:6 salt), can be isolated from solution when a melt of tanalum pentoxide with sodium hydroxide is treated with water. Sodium hexatantalate forms lamellar crystals and is characterized by low solubility in the presence of excess alkali. Jander and Schulz [3] obtained a salt of the same external appearance by adding sodium hydroxide in the cold to a solution prepared by leaching a melt of tantalum pentoxide and potassium hydroxide with water. One of us found that the composition of the salt corresponds to the pentatantalate: $7Na_2O \cdot 5Ta_2O_5 \cdot 40H_2O$ (7:5 salt). The indicated authors obtained a different crystallohydrate when they added a hot solution of sodium hydroxide to a boiling aqueous solution of a melt of tantalum pentoxide with potassium hydroxide, having the form of fine needles. According to their data, it differs from the preceding compound by having a lower water content and corresponded to the formula $7Na_2O \cdot 5Ta_2O_5 \cdot 22H_2O$.

As a result, some authors consider the salt with the lamellar form to be sodium hexatantalate, and others consider it to be the pentatantalate. The present study was initiated to elucidate this problem.

The starting tantalum pentoxide was obtained by the ignition of finely cut tantalum plate in the air. Analysis of the preparation, made by chemical, spectral and x-ray spectral methods, revealed that it contained about 1% niobium and 0.1% titanium.

We obtained the sodium tantalates from a melt of tantalum pentoxide with sodium hydroxide, prepared with a 1:5 weight ratio of Ta_2O_5 to NaOH. After grinding in a mortar, the cold melt was treated with a 10-fold amount of cold water to remove excess alkali and then it was dissolved in water heated to 80°. The solution was filtered and evaporated at 50° to incipient crystallization. The salt separating under these conditions had the form of hexagonal plates with unequal sides (Fig. 1).

For its analysis the salt was dissolved in water. The addition of sulfuric acid until the solution showed weakly acid to methyl red gave a precipitate of tantalic acid. After ignition it was weighed as Ta_2O_5. The filtrate was evaporated to determine sodium as the sulfate. We determined the water by the direct method in a Penfield tube, and at times we determined it by difference.

Analysis of Lamellar Sodium Tantalate

Found %: Na_2O 13.38, 13.18; Ta_2O_5 70.70, 70.92; H_2O 15.92, 15.90 (diff.) 16.70 $8Na_2O \cdot 6Ta_2O_5 \cdot 33H_2O$. Calculated %: Na_2O 13.26; Ta_2O_5 70.85; H_2O 15.89. $8Na_2O \cdot 6Ta_2O_5 \cdot 25H_2O$. Calculated %: Na_2O 13.70; Ta_2O_5 73.69; H_2O 12.52.

The analysis results correspond to the formula of sodium hexatantalate, $8Na_2O \cdot 6Ta_2O_5 \cdot 33H_2O$. Complete agreement of the found amount of sodium oxide and tantalum pentoxide with theory for the hexatantalate is observed if the analysis results are calculated on the basis of the anhydrous salt.

Found %: Na_2O 15.75; Ta_2O_5 84.25. $8Na_2O \cdot 6Ta_2O_5$. Calculated %: Na_2O 15.76; Ta_2O_5 84.24.

We obtained the other salt from an aqueous solution of the starting melt by adding a 0.1N sodium hydroxide solution in the cold. The precipitate obtained here consisted of fine needlelike crystals, which under the microscope revealed a prismatic shape (Fig. 2).

Analysis of Needlelike Sodium Tantalate

Found %: Na_2O 14.17, 14.05; Ta_2O_5 73.04, 73.17; H_2O 12.70, 12.78 (by difference), 13.25. $7Na_2O \cdot 5Ta_2O_5 \cdot 22H_2O$. Calculated %: Na_2O 14.28; Ta_2O_5 72.69; H_2O 13.03.

The preparation was analyzed by the above-described method. The results show that in its composition the needlelike salt closely approaches that of the sodium pentatantalate, $7Na_2O \cdot 5Ta_2O_5 \cdot 22H_2O$. Good agreement of the found amount of oxides with that calculated for sodium pentatantalate is observed when the analysis results are calculated on the basis of the anhydrous salt:

Found %: Na_2O 16.18; Ta_2O_5 83.82. $7Na_2O \cdot 5Ta_2O_5$. Calculated %: Na_2O 16.42; Ta_2O_5 83.58.

Sodium pentatantalate can also be obtained by evaporating an aqueous solution of the melt at a temperature above 85°. Apparently, here an influence is exerted by the increase in concentration of the residual free alkali from the starting melt. In this case the salt again deposits in the form of prisms, but this time of sufficient size to be seen without a microscope (Fig. 3).

As a result, depending on the excess alkali concentration and temperature conditions, it is possible to obtain two different compounds, namely sodium pentatantalate and hexatantalate from an aqueous solution of a melt of tantalum pentoxide with sodium hydroxide.

TABLE 1

Properties of Sodium Tantalate Hydrates

Composition of the Compounds	Crystal form	d^{20}	Index of refraction	pH* of a % solution
$8Na_2O \cdot 6Ta_2O_5 \cdot 33H_2O$	Plates	3.58	n_g 1.644, n_p 1.637	8.58
$7Na_2O \cdot 5Ta_2O_5 \cdot 22H_2O$	Prisms	3.78	n_{m_1} 1.65	8.48

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* Measured with a glass electrode.

TABLE 2

Values of Interplanar Distances in the Lattices of Sodium Tantalate Hydrates

Sodium hexatantalate				Sodium pentatantalate			
Line Nos.	Relative intensity	ϑ°	d(Å)	Line Nos.	Relative intensity	ϑ° '	d(Å)
1	5	7°30′	7.402	1	2	14°27′	3.872
2	2	11 6	5.019	2	3	17 42	3.178
3	4	14 21	3.898	3	4	19 36	2.880
4	2	14 42	3.807	4	2	22 30	2.525
5	2	16 3	3.495	5	2	24 18	2.348
6	2	17 36	3.195	6	3	26 15	2.184
7	1	18 6	3.110	7	3	27 45	2.075
8	5	18 42	3.014	8	1	30 24	1.909
9	3	19 48	2.852	9	1	31 24	1.854
10	2	21 36	2.625	10	2	35 24	1.668
11	4	23 12	2.453	11	2	37 21	1.592
12	4	26 24	2.173	12	1	39 24	1.522
13	2	27 21	2.103	13	3	41 18	1.464
14	2	28 48	2.005				
15	2	30 21	1.912				
16	5	34 3	1.725				
17	2	34 24	1.710				
	(wide bands)	36 12	1.636				
18	2	36 54	1.609				
	(wide bands)	38 24	1.555				
19	1	39 12	1.529				
	(wide bands)	40 24	1.491				
20	3	42 0	1.440				

The lines are somewhat diffuse

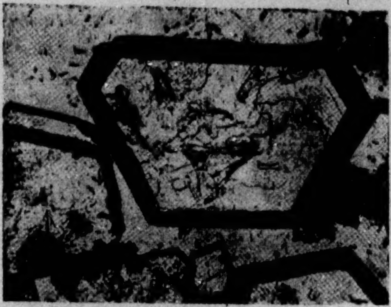

Fig. 1. Sodium hexatantalate, $8Na_2O \cdot 6Ta_2O_5 \cdot 33H_2O$ (x 85).

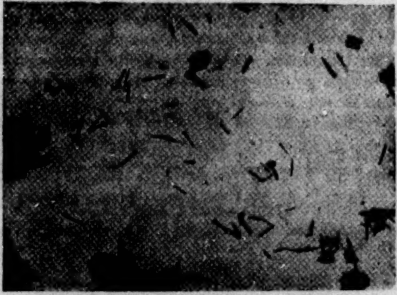

Fig. 2. Sodium pentatantalate, $7Na_2O \cdot 5Ta_2O_5 \cdot 22H_2O$ (x 145).

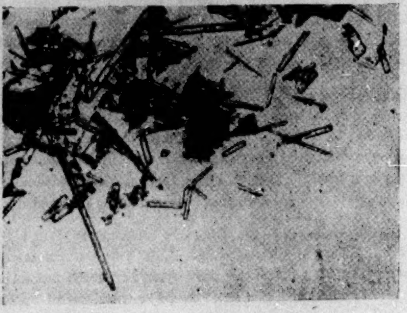

Fig. 3. Sodium pentatantalate, isolated above 85° (x145).

A number of physical constants were determined for the indicated salts, a part of which are given in Table 1. The x-ray study results by the powder method are shown in Table 2 and Fig. 4.

As a result, the studied compounds differ in their physical properties. In addition, the process for their dehydration also proceeds differently.

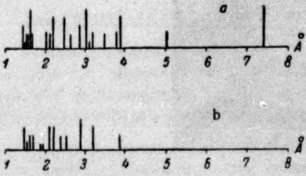

Fig. 4. Interplanar distances in the lattices of sodium tantalate hydrates – $8Na_2O \cdot 6Ta_2O_5 \cdot 33H_2O$ (a) and $7Na_2O \cdot 5Ta_2O_5 \cdot 22H_2O$ (b).

E. E. Flint [4] used a goniometer to study the coarse sodium hexatantalate crystals obtained by us. Here it was shown that the salt belongs to the hexagonal syngony; class $L^6 6L^2 7PC$, a: c = 0.7275; forms a simple, pinacoid (0001) and hexagonal dipyramid (1121).

SUMMARY

1. Depending on the preparation conditions, it is possible to isolate both sodium hexatantalate and pentatantalate from an aqueous solution of a melt of tantalum pentoxide with sodium hydroxide.

2. Sodium hexatantalate, $8Na_2O \cdot 6Ta_2O_5 \cdot 33H_2O(Na_2O : Ta_2O_5 = 1.33)$ is isolated as lamellar crystals from an aqueous solution of a tantalum pentoxide-sodium hydroxide melt.

3. Sodium pentatantalate, $7Na_2O \cdot 5Ta_2O_5 \cdot 22H_2O(Na_2O : Ta_2O_5 = 1.4)$ deposits from the above-indicated solution as fine prismatic crystals when a more alkaline medium is used.

4. Data are presented for some of the physical properties of the obtained salts.

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Received July 18, 1955

Institute of Physical Chemistry, Academy of Sciences of the USSR

MECHANISM FOR THE REACTION OF TANTALUM PENTOXIDE WITH SODIUM HYDROXIDE

Vikt. I. Spitsyn and N. N. Shavrova

Alkaline tantalates are formed when tantalum pentoxide and tantalum-containing minerals are fused with caustic alkalies. It is assumed that the composition of these tantalates corresponds to the meta-salts. Thus, Smithels [1] gives the following equation for the fusion reaction of the mineral tantalite with potassium hydroxide:

$$2KOH + FeTa_2O_6 = K_2Ta_2O_6 + FeO + H_2O.$$

N. M. Zarubin and A. N. Koptsik [2] believe that the fusion product of tantalite with sodium hydroxide is sodium metatantalate, $NaTaO_3$. However, it is known that the normal metatantalates of the alkali elements are practically insoluble in water. Salts of more complex composition, for example $Na\ Ta_5O_{16}$, $Na_8Ta_6O_{19}$ [3] or $K_8Ta_6O_{19}$ go into solution as the corresponding hydrates when the above-indicated alkaline melts are treated with water. If the metatantalate is present in the melt, then the formation of similar compounds could be explained only by reaction of the metatantalate with sodium hydroxide solution, for example, in the following manner [4]:

$$6NaTaO_3 + 2NaOH + 32H_2O = Na_8Ta_6O_{19} \cdot 33H_2O.$$

However, the experimental verification made by us failed to support this postulation.

Anhydrous sodium metatantalate, $NaTaO_3$, was obtained by the ignition of the hydrates at 900° – the hexatantalate $8Na_2O \cdot 6Ta_2O_5 \cdot 33H_2O$ and the pentatantalate $7Na_2O \cdot 5Ta_2O_5 \cdot 22H_2O$, followed by treatment with distilled water to completely remove any free alkali. The dried product was analyzed by fusion with potassium pyrosulfate. Tannin was used to isolate the tantalum. The obtained preparations contained 87.33 and 87.36% Ta_2O_5 (calculated for $NaTaO_3$, 87.69% Ta_2O_5).

Samples of the anhydrous sodium metatantalate, weighing from 0.1 to 0.3 g, were treated with 10 ml portions of sodium hydroxide solution of variable concentration on the boiling water bath for 1 hour. After cooling, the insoluble precipitate was filtered, washed with water until excess alkali was completely removed, dried, ignited, and weighed. For comparison, a similar treatment of the metatantalate with water was made.

From the experimental results given in Table 1 it is evident that the solubility of sodium metatantalate in water is slight and that it fails to show essential change in the presence of sodium hydroxide. The practically constant weight of the taken salt, both before and after its treatment with alkali solution, permits concluding that the formation of some new insoluble sodium tantalates also fails to occur here. As a result, it can be assumed that the anhydrous metatantalate fails to react with sodium hydroxide solutions. Evidently, not the metatantalate, but some other compound is present in the melts of tantalum pentoxide with caustic alkalies.

To elucidate this problem, a melt of tantalum pentoxide with sodium hydroxide, prepared with a 1:5 weight ratio of the components, was leached with small portions of anhydrous alcohol at the boil. The treatment was continued until all unreacted alkali had been removed. The alcohol-insoluble residue was dried at 110°. The acid method was used for its analysis. We give below the composition of the reaction product of tantalum pentoxide with sodium hydroxide, insoluble in anhydrous alcohol.

Found %: Ta_2O_5 60.07 (Expt. 1), 59.65 (Expt. 2). Na_5TaO_5. Calculated %: Ta_2O_5 58.77. Na_3TaO_4. Calculated %: Ta_2O_5 70.37. $NaTaO_3$. Calculated %: Ta_2O_5 87.69.

TABLE 1
Treatment of Sodium Metatantalate with Water and with NaOH Solutions

Expt. No.	Weight of salt (g)		Change in weight (g)	Solvent
	before treatment	after treatment		
1	0.2376	0.2369	—0.0007	Water
2	0.3548	0.3540	—0.0008	Water
3	0.1827	0.1822	—0.0005	0.01 N NaOH
4	0.1547	0.1552	+0.0005	0.1 N NaOH
5	0.1095	0.1090	—0.0005	1 N NaOH

It can considered as established that in the melts of tantalum pentoxide with excess sodium hydroxide there is also present a new compound – sodium orthotantalate of composition Na_5TaO_5. Evidently, its formation proceeds by the following equation:

$$10NaOH + Ta_2O_5 = 2Na_5TaO_5 + 5H_2O.$$

The obtained compound has a grayish color and consists of very fine crystals, which form small aggregates. When microphotographed (Fig. 1) the latter appear as small opaque clumps. The index of light refraction of the crystals was found to lie in the limits 1.600-1.610. The melting point of the salt is 1030°. The specific gravity, determined in ethyl alcohol, is 2.58 at 20°. In Table 2 and Fig. 2 the debyegrams of the interplanar distances in the crystals of compounds $NaTaO_3$ and Na_5TaO_5 are compared. The observed structures are completely different.

The salt Na_5TaO_5 is soluble in water, but from its solution there separate prismatic crystals of sodium pentatantalate, $Na_7Ta_5O_{16} \cdot 11H_2O$. Evidently, when introduced into water the sodium orthotantalate shows hydrolysis:

$$5Na_5TaO_5 + 20H_2O = Na_7Ta_5O_{16} \cdot 11H_2O + 18NaOH.$$

As a result, when a melt of tantalum pentoxide with sodium hydroxide is treated with water there proceeds, not direct solution of the compound Na_5TaO_5 present in the melt, but instead its hydrolysis and hydration of the resulting less basic tantalate. A similar reaction mechanism was established by V. I. Spitsyn and A. V. Lapitsky [5] for the reaction of niobium pentoxide with sodium hydroxide.

Fig. 1. Sodium orthotantalate Na_5TaO_5 (x 145)

TABLE 2

Values of Interplanar Distances in the Lattices of Anhydrous Sodium Tantalates

$NaTaO_3$				Na_5TaO_5			
Line Nos.	Relative intensity	V	d(Å)	Line Nos.	Relative intensity	V	d(Å)
1	1	12°53′	4.311	1	2	17°54′	3.144
2	4	14 30	3.859	2	3	18 36	3.029
3	1	15 42	3.571	3	2	19 30	2.894
4	2	18 45	3.006	4	4	21 36	2.625
5	1	20 42	2.733	5	3	23 30	2.423
6	3	25 36	2.236	6	1	24 12	2.357
7	2	26 45	2.146	7	3	25 30	2.244
8	2	28 45	2.035	8	2	26 06	2.196
9	4	29 48	1.944	9	3	28 39	2.015
10	2	30 12	1.921	10	1	30 27	1.906
11	5	33 51	1.734	11	1	33 18	1.760
12	5	37 36	1.583	12	3	33 54	1.732
13	1	40 06	1.500	13	2	35 48	1.652
14	1	42 30	1.430	14	3	37 21	1.592
15	4	44 36	1.376	15	2	39 30	1.519
16	1	45 15	1.360	16	2	41 48	1.449
17	5	48 09	1.297	17	1	46 48	1.325
18	5	51 42	1.231				
19	4	55 24	1.184				
20	2	57 24	1.147				
21	3	59 21	1.123				
22	5	63 27	1.080				

The reaction of aqueous sodium hydroxide solutions with tantalum pentoxide results in the direct formation of sodium pentatantalate, which appears as prismatic crystals of the salt $Na_7Ta_5O_{16} \cdot 11H_2O$. The insoluble residue represents unreacted tantalum pentoxide. When treated for 2 hours on the water bath with 0.1N NaOH solution, from 3 to 4% of the taken weight of ignited tantalum pentoxide reacts in the sense of forming the tantalate. Under the same conditions the tantalum pentoxide that is obtained by the treatment of potassium fluotantalate with sulfuric acid, and dried at 110° but not ignited, shows a reaction rate with sodium hydroxide that is approximately 5 times more rapid. It should be mentioned that niobium pentoxide shows much less active reaction with sodium hydroxide solutions [5] than does tantalum pentoxide.

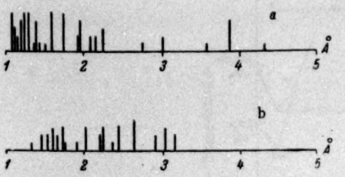

Fig. 2. Interplanar distances in the lattices of anhydrous sodium tantalates – $NaTaO_3$ (a) and Na_5TaO_5 (b).

SUMMARY

1. We studied the reaction of tantalum pentoxide with sodium hydroxide under various conditions and of sodium metatantalate with NaOH solutions.

2. The tantalate of composition Na_5TaO_5 is formed when tantalum pentoxide is fused with sodium hydroxide. This compound, when dissolved in water, shows hydrolysis and is transformed into the pentatantalate – $Na_7Ta_5O_{16} \cdot 11H_2O$.

3. Some of the constants of sodium orthotantalate – Na_5TaO_5 – were determined.

4. Tantalum pentoxide reacts with aqueous sodium hydroxide solutions to yield sodium pentatantalate – $Na_7Ta_5O_{16} \cdot 11H_2O$. The reaction rate depends on the temperature conditions used to prepare the Ta_2O_5.

5. Anhydrous sodium metatantalate, $NaTaO_3$, fails to react with aqueous NaOH solutions.

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Received July 18, 1955

Institute of Physical Chemistry, Academy of Sciences of the USSR

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REACTION OF SODIUM AND POTASSIUM METATITANATES WITH SALTS IN MELTS

M. L. Sholokhovich and G. V. Barkova

In connection with the exclusively interesting and practically important seignettoelectric properties shown by barium and lead titanates [1,2] it seemed of interest to study the physicochemical properties of various metallic titanates.

In this paper we give the results of studying the binary systems composed of sodium and metatitanates and chlorides, oxygen-containing salts of the MeO_4'' type,* pyrophosphates or metavanadates in melts. The reaction between sodium and potassium metatitanates, and between sodium and potassium metatitanates and fluorides, was described earlier [3].

EXPERIMENTAL

The study was made using the visual-polythermal fusion method. The method used to prepare the sodium and potassium metatitanates has already been described [3]. The sodium and potassium metavanadates were obtained by the fusion of the corresponding carbonates with vanadium pentoxide, taken in stoichiometric proportions; potassium tungstate and molybdate were obtained by the fusion of WO_3 and MoO_3 with the corresponding carbonates; the remaining salts were of pharmacopeia quality, previously purified by recrystallization. All of the data are expressed in equimolar percents.

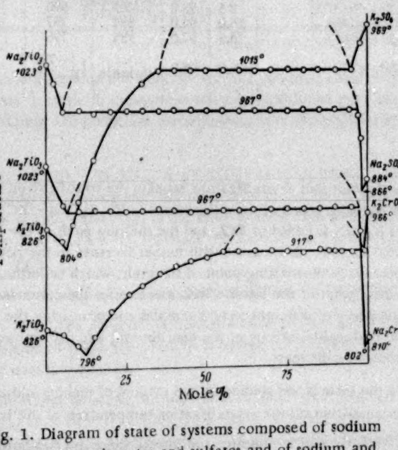

Fig. 1. Diagram of state of systems composed of sodium potassium metatitanates and sulfates and of sodium and potassium metatitanates and chromates.

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* $MeO_4'' - SO_4''$, CrO_4'', MoO_4'', WO_4''.

Systems Composed of Metatitanates and Salts of Type K_2MeO_4 or Na_2MeO_4.

The systems studied were: Na_2TiO_3 - Na_2SO_4, K_2TiO_3 - K_2SO_4, Na_2TiO_3 - Na_2CrO_4, K_2TiO_3 - K_2CrO_4, Na_2TiO_3 - Na_2MoO_4, K_2TiO_3 - K_2MoO_4, Na_2TiO_3 -Na_2WO_4, K_2TiO_3 - K_2WO_4.

The obtained data are given in Table 1 and plotted in Figs. 1 and 2. In all of the enumerated systems there exists limited solubility in the liquid state, in which connection all of the sodium systems show wider stratification zones than do the corresponding potassium systems. In the sodium systems there is crystallization of sodium metatitanate beneath the stratification region, and of K_2MeO_4 in the potassium systems.

Systems Composed of Sodium and Potassium Metatitanates and Chlorides.

Stratificiation is also present in the systems Na_2TiO_3 - Na_2Cl_2 and K_2TiO_3 - K_2Cl_2 (Table 1, Fig. 3). There is monotectic stratification in the system Na_2TiO_3 - Na_2Cl_2, while the system K_2TiO_3 - K_2Cl_2 shows especial interest. When the latter was studied in the direction from KCl to K_2TiO_3 it was established that stratification begins even at a 2% content of K_2TiO_3 in the melt, and extending to 75% K_2TiO_3. The lower layer of the melt crystallizes as well-formed slender needles.. The crystallization temperatures of the two layers of the melt are so different that it is a very easy matter to separate the two layers. Crystallization of the phases beneath the stratification region proceeds at variable temperatures.

TABLE 1

(Character of Reaction for the Enumerated Systems – Stratification)

Expt. Nos.	System	Stratification interval (in mole %) for added component		Temperature of monotectic stratification	Temperature of the eutectic point	Contents of added component at the eutectic point (in mole %)	Phase showing crystallization beneath the stratification region
		from	to				
1	Na_2TiO_3—Na_2SO_4	5.0	97.0	967°	866°	98.5	Na_2TiO_3
2	K_2TiO_3—K_2SO_4	35	95.0	1015	804	6.0	K_2SO_4
3	Na_2TiO_3—Na_2CrO_4	6.5	98.0	967	802	99.5	Na_2TiO_3
4	K_2TiO_3-K_2CrO_4	55.0	99.0	917	796	12.0	K_2CrO_4
5	Na_2TiO_3—Na_2MoO_4	6.0	97.0	977	682	99.5	Na_2TiO_3
6	K_2TiO_3—K_2MoO_4	40.0	99.0	917	786	17.0	K_2MoO_4
7	Na_2TiO_3—Na_2WO_4	2.5	93.0	961	696	99.5	Na_2TiO_3
8	K_2TiO_3—K_2WO_4	25.0	94.0	884	787	19.0	K_2WO_4
9	Na_2TiO_3—Na_2Cl_2	13.5	97.0	933	796	99.0	Na_2TiO_3
10	K_2TiO_3—K_2Cl_2	25.0	98.0	Variable	I—792* II—770	98.5	$K_2Ti_3O_7$

Of exceeding interest is the fact that crystallization beneath the stratification region proceeds at temperatures that are higher than the melting points of the components in the K_2TiO_3 - KCl system. Thus, there is stratification when only 2% of K_2TiO_3 is added to KCl, and the melting point of the melt rises sharply from 774° (melting point of pure KCl) to 884°. In measure with further increase in the potassium metatitanate concentration there is gradual decrease in the melting point of the melt, which nevertheless, up to 70% K_2TiO_3, always remains above the melting point of the latter. Such a course for the curve was obtained under the conditions of studying systems composed of different weight samples and of heating the melt only once. Repeated heating of the melt resulted in noticeable shifting of the equilibrium, and the temperature when the first crystals appeared for the given melt showed a decrease.

As a result of this, when the system was studied by the method of making additions, the curve shows some shifting, both as regards the composition and the crystallization temperatures of the melts, but its general character is retained. The quantitative proportions of the elements, entering into the composition of the substance showing crystallization beneath the stratification region, was determined by spectral analysis.* On the basis of these data it was established that the substance crystallizing beneath the stratification region is potassium trititanate $K_2Ti_3O_7$.

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* The system K_2TiO_3 - K_2Cl_2 fails to show a eutectic, and instead there are two points of intersection for the curves of different phases.

Systems Composed of Sodium and Potassium Metatitanates and Metavanadates and of Sodium and Potassium Metatitanates and Pyrophosphates

In contrast to the above described systems, sodium and potassium metatitanates show unlimited solubility in melts of sodium and potassium metavanadates and pyrophosphates.

The crystallization curve in the system Na_2TiO_3-$(NaVO_3)_2$ consists of three branches (Table 2, Fig. 4). The second branch at 1046° shows a well-defined maximum, approximately corresponding to a 1:1 composition.

The crystallization curve in the system K_2TiO_3-$(KVO_3)_2$ consists of four branches (Table 2, Fig. 4). One of the crystallization branches, also having a 1:1 composition, passes through a maximum at 1006°.

In both cases the melts, corresponding to the curve maxima, fail to show crystallization at a constant temperature. Consequently, in both systems the presence of compounds that could have been expected on the basis of the fusion curves is excluded.

TABLE 2

System	Characterization of the system	Composition and temperature of the points of intersection for the curves of the metatitanates with the TiO_2 curve			
		point *I*		point *II*	
		amount of added component (in mole %)	temperature	amount of added component (in mole %)	temperature
Na_2TiO_3—$(NaVO_3)_2$	Unstable section of the ternary system Na_2O—TiO_2—V_2O_5	20.5	920°	99.5	638°
K_2TiO_3—$(KVO_3)_2$	Unstable section of the ternary system K_2O—TiO_2—V_2O_5	2.00	788	97.5	512

In both cases a phase crystallizes on the branches showing maxima, externally appearing as titanium dioxide. The presence of a TiO_2 phase as rutile in these melts was also established by x-ray analysis.** Evidently, in metavanadate melts both sodium and potassium metatitanates show decomposition with the separation of a solid TiO_2 phase.

As a result, the systems Na_2TiO_3 - $(NaVO_3)_2$ and K_2TiO_3 - $(KVO_3)_2$ do not appear as binary systems in melts. Instead, they should be considered as being unstable sections of the ternary systems Me_2O - TiO_2 - V_2O_5 (Me = Na or K) (Fig. 5). The section $NaTiO_3$ - $(NaVO_3)_2$ in the interval from 20.5 to 99.5% $NaVO_3$ and the section K_2TiO_3 - $(KVO_3)_2$ in the interval from 2 to 97.5% KVO_3 intersect the field of the starting TiO_2 component in the plane of the triangle Me_2O - TiO_2 - V_2O_5.

The obtained data are found in agreement with the postulations expressed by N. S. Dombrovskaya [4].

In the system K_2TiO_3 - $(KVO_3)_2$ a phase shows crystallization in the interval from 2% KVO_3 and 788° to 20% KVO_3 and 820°, the composition of which we failed to investigate. It is possible that this phase represents polymorphous transformation of titanium dioxide.

Due to the high melting points involved, we were able to make only a partial study of the system (Na_2TiO_3)

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* The spectral analysis was made by A. S. Nakonechny in the Spectral Analysis Laboratory of the Rostov State University.

** The x-ray phase analysis was made by E. G. Fesenko in the x-Ray Laboratory of the Scientific-Research Physical-Mathematical Institute of the Rostov State University.

$-Na_4P_2O_7$ (Fig. 4). Here the curve is also composed of three branches. The composition of the phase, crystallizing on the branch with a maximum, was not investigated.

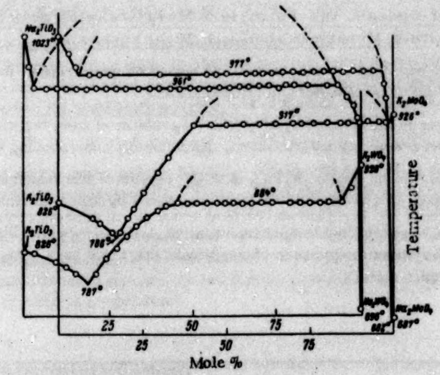

Fig. 2. Diagram of state of systems composed of sodium and potassium metatitanates and tungstates and sodium and potassium metatitanates and molybdates.

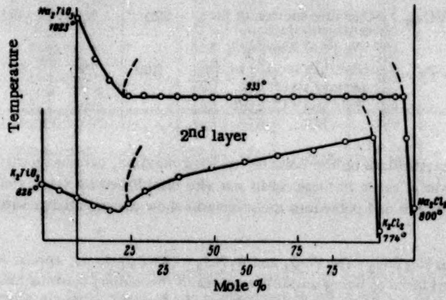

Fig. 3. Diagram of state of systems composed of sodium and potassium metatitanates and chlorides.

DISCUSSION OF RESULTS

A study of the fusion of binary systems composed of sodium and potassium metatitanates with various salts revealed that both sodium and potassium metatitanates differ from $BaTiO_3$ by showing a considerably greater solubility in salt melts.

Barium titanate is very difficultly soluble in most salt melts [5]. The sodium and potassium titanates show considerably greater solubility, but in this connection they show only limited solubility in many salts, in the liquid state forming systems with stratification.

Whereas the phenomenon of stratification on a stable diagonal of ternary reciprocal systems of AX + BY ⇌ AY + BX type is well known, up to now only several cases of stratification in binary systems of either type AX - AY or BX - AX have been known, and specifically, in the systems: Na_2Cl_2 - $Na_2B_4O_7$ [6], K_2Cl_2 - $K_2B_4O_7$[6], Na_2SO_4 - $Na_2B_4O_7$ [7].

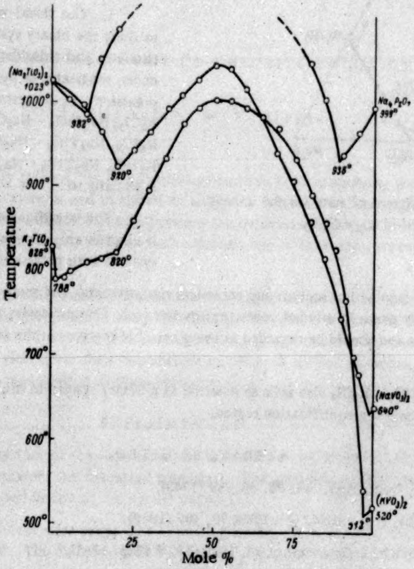

Fig. 4. Diagram of state of systems composed of sodium and potassium metatitanates and metavanadates and of sodium and potassium metatitanates and pyrophosphates.

Here we also present data on still another 10 binary systems that show stratification. We established that the sodium and potassium metatitanates form binary systems showing stratification with chlorides and all oxygen-containing salts of the type of either K_2MeO_4 or Na_2MeO_4.

The tendency for stratification is clearly manifested in our earlier studied system Na_2TiO_3-Na_2F_2, while in the system Na_2TiO_3-K_2TiO_3, together with complex-formation, the possibility of stratification is not excluded [3].

As a result, a study of the fusion of binary systems composed of sodium and potassium metatitanates with various sodium and potassium salts revealed that one of their characteristic properties is the limited solubility in the liquid state shown by sodium and potassium metatitanates in the chlorides and oxygen-containing sodium and potassium salts whose anions belong to the 6th group of the periodic system ($SO_4^=$, $CrO_4^=$, $MoO_4^=$, $WO_4^=$).

The study made by us also indicates the tendency shown by the sodium and potassium metatitanates to suffer decomposition under the influence of a third component with the separation of a solid TiO_2 phase. This is very clearly seen in the systems with the sodium and potassium vanadates and in the system with potassium chloride.

A very interesting fact takes place in the system K_2TiO_3 - K_2Cl_2, where, instead of the components of the system, $K_2Ti_3O_7$ shows crystallization beneath the stratification region. As a result, the system K_2TiO_3 - K_2Cl_2 fails to appear as a binary system in melts. Apparently, in a KCl melt and under its influence, potassium metatitanate shows partial decomposition with the separation of titanium dioxide. The latter reacts with the K_2TiO_3

remaining in the melt to give $K_2Ti_2O_7$, which then crystallizes when the system is cooled. This supports the opinion expressed earlier by I. N. Belyaev on stratification processes [8].

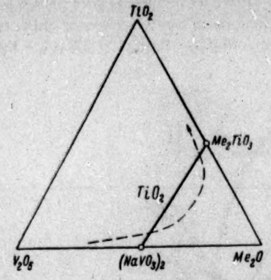

Fig. 5. Scheme of the diagram of state for the ternary system composed of Me_2O - TiO_2 - V_2O_5.

SUMMARY

1. The visual-polythermal method was used to study the binary systems composed of the metatitanates and chlorides, sulfates, chromates, molybdates, tungstates or pyrophosphates of sodium and potassium. In the systems Na_2TiO_3 - Na_2Cl_2, K_2TiO_3 - K_2Cl_2, Na_2TiO_3 - Na_2CrO_4, K_2TiO_3 - K_2CrO_4, K_2TiO_3 - K_2SO_4, Na_2TiO_3 - Na_2SO_4, Na_2TiO_3 - Na_2WO_4, K_2TiO_3 - K_2WO_4, Na_2TiO_3 - Na_2MoO_4, K_2TiO_3 - K_2MoO_4 there is stratification in a wide concentration interval.

The stratification region in the sodium systems is considerably broader than in the corresponding systems with potassium salts.

2. In the systems composed of sodium and potassium metatitanates and metavanadates there is separation of a solid titanium dioxide phase in a broad concentration interval. Consequently, the given systems fail to appear as binary systems in melts and should be regarded as bring unstable sections of the ternary systems Me_2O - TiO_2 - V_2O_5.

3. The system K_2TiO_3 - K_2Cl_2 also fails to function as a binary system in melts, since the compound $K_2Ti_2O_7$ shows crystallization beneath the stratification region.

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Received May 19, 1955

Rostov-on-Don State University

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* T.p. = C. B. Translation pagination.

POTENTIOMETRIC STUDY OF CHLORITE SOLUTIONS

E. I. Flis and T. M. Vasilyeva

The potentiometric study method has found wide application, both in studying the chemical and physicochemical properties of various systems and in chemical analysis. It was shown earlier [1,2] that this method permits characterizing the relationship that exists between the oxidation potentials of hypochlorite solutions and the pH, and also makes it possible to analyze such solutions and to follow the processes that prevail in them.

Methods on the potentiometric analysis of chlorites in solution are described in the literature [3-5], and also some data on the oxidation potentials of these systems [6]. However, as far as we know, the potentiometric method has not been used to study the processes that take place in chlorite solutions; neither have the oxidation potentials of these systems nor their dependence on pH been studied in detail, for which reason the present work is devoted to an examination of these problems.

EXPERIMENTAL

A glass electrode was used in all the experiments to measure the pH of the solutions, while a platinum gauze electrode was used to measure the oxidation potentials. The apparatus used to make the potentiometric measurements has been described in one of our earlier papers [1].

Sodium and barium chlorites were prepared by reacting freshly prepared chlorine dioxide with sodium and barium peroxides, respectively. The chlorine dioxide needed for this was prepared in the usual manner from c.p. potassium chlorate, oxalic acid and sulfuric acid. The chlorine dioxide was purified by condensing it in a dark flask. The obtained chlorite solutions failed to contain either chlorates or chlorides, which testifies to the absence of chlorine in the starting chlorine dioxide solutions. The sodium chlorite solution contained a certain amount of soda, while the barium chlorite solution contained some free alkali.

In the first experiments we elucidated the possibility of determining the amount of alkali and soda in the chlorite solutions by the potentiometric titration method, which was run in a beaker wrapped with black paper. The solution used for titration (0.1N H_2SO_4) was added in portions to a definite volume of the chlorite solution (50 ml). The solution was shaken vigorously after each addition. All of the experiments were run at 18-20°. The potentiometric titration results are plotted in Fig. 1. We observe two inflection points on Curve I (Fig. 1). The first one corresponds to completion of the reaction: $CO_3^{2-} + H^+ \rightarrow HCO_3^-$, and the second one to the reaction: $HCO_3^- + H^+ \rightarrow H_2CO_3(CO_2)$. Analysis of Curve I reveals that the sodium chlorite solution fails to contain any free alkali. Based on the potentiometric analysis data, the total amount of soda is $10.7 \cdot 10^{-4}$ g-equiv. These data show good agreement with the values obtained by titration in the presence of methyl orange ($10.8 \cdot 10^{-4}$ g-equiv.).

For determining the mutual amount of alkali and soda in such solutions as contain either hypochlorites or chlorites the potentiometric method is uniquely desirable, since the method used for ordinary solutions, namely a double titration with phenolphthalein and methyl orange (giving extremely inaccurate results), is completely unsuitable in the given case due to decomposition of the phenolphthalein by the oxidizing agent [7,8].

Curve II (Fig. 1) characterizes the change in pH when the barium chlorite is titrated, and from it the amount of alkali can be easily and quite accurately determined. As can be seen from an analysis of this curve,

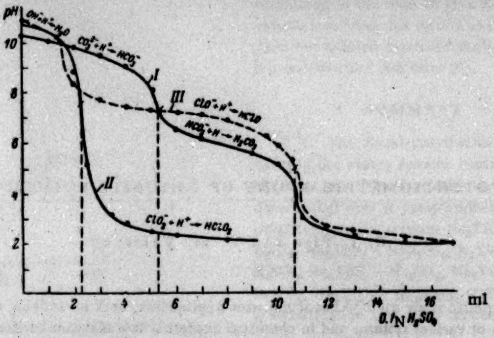

Fig. 1. Curves for the potentiometric titration of sodium chlorite (I), barium chlorite (II) and sodium hypochlorite (III) with acid.

the barium chlorite solution contained $2.3 \cdot 10^{-4}$ g-equiv. of free alkali in 50 ml of solution. The lower portion of Curves I and II coresponds to the formation of chlorous acid, $ClO_2^- + H^+ \rightarrow HClO_2$, and lies at pH < 3. A similar process for the formation of hypochlorous acid, $ClO^- + H^+ \rightarrow HClO$, takes place at a considerably higher pH value, approximately equal to 8.5-6.5.

The character of pH change when the hypochlorite is titrated with acid is shown on Curve III (Fig. 1). The position of the portions, characterizing the process $A^- + H^+ \rightarrow HA$, clearly illustrates the electrolytic properties of $HClO$, H_2CO_3, $HClO_2$; the position of curves in Fig. 1 shows that $HClO_2$ is a considerably stronger acid than either carbonic or hypochlorous acid.

Observations made on the color of the titrated solution revealed that the formation of appreciable amounts of ClO_2 in the chlorite solution begins at pH values of about 5-6. The lower the pH of the solution, the more intense is the green color, determined by the existence of chlorine dioxide in the solution.

The purpose of further experimentation was to establish the possibility of using the potentiometric method to study the different processes that take place in chlorite solutions at different pH values. For this we ran a potentiometric titration with alkali of definite amounts of chlorite, made acid with 17 ml of 0.1N sulfuric acid. The results of these experiments are shown in Fig. 2, where Curve II characterizes the process immediately after adding the acid, Curve III – after the lapse of 4 hours, and Curve IV – after 16 hours. For comparison we show the curve for the potentiometric titration of the starting chlorite solution with sulfuric acid (I).

The character of the curves and their relative position makes it possible to follow the changes that take place in the acidified chlorite solution. Curves II-IV are shifted with respect to Curve I. Apparently, in acid medium a portion of the chlorous acid is converted into chlorine dioxide, which is supported in all of the experiments by the green color of the solution. The distance a along the abscissa characterizes the amount of $HClO_2$ that underwent conversion, in which connection it shows increase with increase in the time of remaining in an acid medium. This suggests that the conversion of $HClO_2$ is a function of time; to be sure, this process is more rapid immediately after acidification.

The curves also show that with time the carbon dioxide that is formed here escapes by volatization from the acid solution. If the back titration with alkali is made immediately after acidification, then hardly any loss of carbon dioxide is observed (portions b and c). The amount of carbon dioxide in solution shows considerable decrease in 4 hours after acidification, and the decrease is even greater after 16 hours (portion d). At the end of titration, despite achieving a strongly alkaline medium, the solution remains green-colored, characteristic for chlorine dioxide.

As a result, it follows from our experiments that with the aid of the curves for the potentiometric titration of chlorite solutions with either acids or alkalies it becomes possible to study the character and rate of the changes that take place in them. However, a complete study of these processes requires the simultaneous coupling of several methods, as a result of which the potentiometric method should first of all be supplemented by a carefully developed chemical analysis.

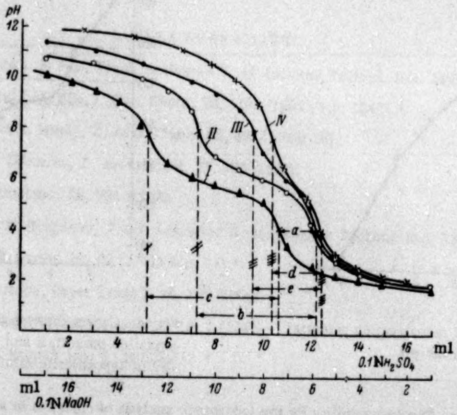

Fig. 2. Curves for the titration of chlorite solution with acid and the back titration with alkali after different time intervals.

I) Direct titration of the sodium chlorite solution with acid; II) back titration of the acid solution with alkali immediately after adding the acid; III) and IV) back titration of the acid solution with alkali after 4 and 16 hours, respectively.

We had already indicated above that the solution pH of oxygen-containing chlorine compounds shows considerable influence on both the processes that take place here and the oxidation properties of such systems. This is shown very convincingly on the example of hypochlorites [1,9,10]. The pH value should fail to exert any lesser influence on the oxidation potentials of chlorite and chlorine dioxide solutions. Since in the titration of chlorite solutions the experimental conditions used do not permit rapid determination of fully established oxidation potential values, we undertook the problem of measuring the oxidation potentials in chlorite solutions at various pH values and under prolonged observation. Here the problem was to study the relationship existing between the oxidation potentials and the pH values of the solutions. Each measurement lasted several hours, and in some cases they ran for a day. Those values of $\varphi_{\text{ox.}}$ were recorded which remained constant, as a limiting case, for two or three hours. The results of these measurements are shown in Fig. 3.

The curve shown in Fig. 3 characterizes the relationship that exists between the oxidation potential and pH value in a chlorite solution. It can be assumed that it reflects all of the processes that take place in a chlorite solution when it is acidified. As can be seen from the nature of the curve, the relationship between the oxidation potentials and the pH in different pH intervals is subject to sundry rules. With the exception of the portion lying in the approximate pH interval of 4-6 the oxidation potential shows considerable increase with decrease in pH (i.e. with acidification of the solution).

The results obtained by us permit making the conclusion that the oxidation potential of chlorite solutions, and consequently also their oxidation capacity, are strongly dependent on the pH. The lower the pH, the higher the oxidation potential, and with other conditions kept constant, the more intense the oxidation processes should

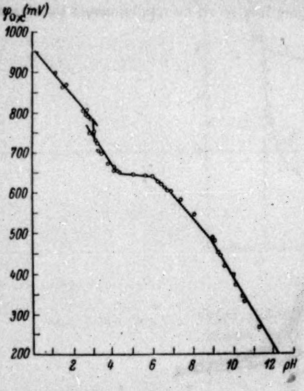

Fig. 3. Dependence of the oxidation potential of chlorite solutions on the pH.

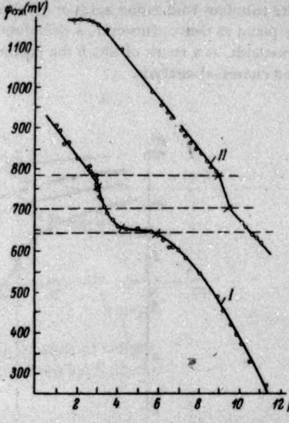

Fig. 4. Curves showing the relationship between oxidation potentials and pH in chlorite solution (I) and in hypochlorite solution (II).

be in chlorite solutions. The impossibility for the iodometric analysis of chlorites in alkaline medium can be explained by these results. Apparently, the oxidation potential of chlorites in alkaline medium is insufficient to oxidize the iodide and favorable conditions for this are created only in acid medium. These results can be used to expalin why it is necessary to acidify chlorite solutions to a pH of 5-6 in the bleaching of cellulose. Apparently, above these pH values the oxidation potential of the solution is below that needed to oxidize the colored substances present in the fiber.

Since the oxidation potential seems to be the most accurate criterion of the oxidation capacity shown by systems, it appears highly profitable to compare the oxidation potentials shown by chlorite and chlorine dioxide solutions with those possessed by hypochlorites and chlorine. Such a comparison can be based on the data shown in Fig. 4, where the curves characterize the change in oxidation potential with pH change in chlorite (I) and hypochlorite (II) solutions. As can be seen from Fig. 4, the curve for the hypochlorite lies above the curve for the chlorite. At the same pH value the oxidation potential in chlorite solutions is on the average 375-350 mV below the potential of the hypochlorite solutions.

From a comparison of the data given in Fig. 4 for the oxidation potentials of hypochlorites and chlorites we see that the oxidation potentials of alkaline hypochlorite solutions (in the pH interval 9.5-10.5) are equal to the oxidation potentials of chlorite solutions in weakly acid medium (in the pH interval 3.5-6). The oxidation potentials of hypochlorite solutions in the pH interval 9.5-9.0 are equal to the oxidation potentials of chlorite solutions in the pH interval 3.5-3.0, etc. From this it can be concluded that the oxidation capacity shown by hypochlorite solutions in the pH interval 9.5-10.5 should be approximately the same as that shown by chlorites in the pH interval 3.5-6. It is known that cellulose shows comparatively little decomposition when it is bleached with hypochlorite in the pH interval 9.5-10.5. At the same time the bleaching of cellulose with chlorite is practically impossible in acid medium, where the value of its oxidation potential is comparable to the oxidation potential shown by hypochlorites in alkaline medium. This corresponds to the data shown in Fig. 4, characterizing the oxidation potentials shown by chlorites and hypochlorites.

SUMMARY

1. We studied the potentiometric titration of chlorite and chlorous acid solutions with both acid and alkali. It was established that considerable amounts of chlorine dioxide are formed in chlorite solutions at pH values close to 6. It was shown that with the aid of potentiometric studies it is possible to follow the changes that take place in a chlorite and chlorous acid solution.

2. The relationship between the oxidation potential of a chlorite solution and its pH was studied in the pH interval from 11 to 2. Based on the results obtained it was shown that the oxidation potential of these systems increases with increase in acidity. These results explain a number of known facts relative to the oxidative action of chlorites.

3. The oxidation potentials of a chlorite and hypochlorite were compared for the first time in a wide pH interval (2-11) and some conclusions were made with respect to the relative oxidation capacity shown by these systems.

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Received June 15, 1955.

Leningrad V. M. Molotov
Technological Institute

THERMOGRAPHIC STUDY OF CHROMIUM SULFATE

I. D. Muzyka and O. I. Shor

Depending on the conditions used to synthesize chromium sulfate various modifications of the latter can be obtained, differing both in the number of moles of crystallization water and in the bond character of the SO_4-group.

Crystallohydrates of chromium sulfate, containing 18, 17, 16 (stable and metastable forms [2]), 15, 14, 12, 9, 3 and 2 moles of crystallization water, have been described in the literature [1]. The last two crystallohydrates were established as being thermal dehydration products.

The violet and green modifications of chromium sulfate are distinguished by the character of the bond between the SO_4-group and chromium.

The violet modification of chromium sulfate has been assigned the formula $[Cr(H_2O)_6]_2(SO_4)_3 \cdot 6H_2O$.

Solutions of the green modifications of chromium sulfate differ from the violet form by a smaller number of coordination-linked water molecules and by the presence of hydroxyl groups in the inner sphere of the complex. Thus, for example, based on the data of Gustavson [3], who studied chromium sulfate solutions, the complexes $[Cr_2(OH)_2SO_4]^{2+}$ and $[Cr_2(OH)_2(SO_4)_2]^0$ were established. Of the various directions given in the literature for the synthesis of the violet form of chromium sulfate the two methods most frequently used are: 1) the synthesis based on the treatment of chrome alum solutions with sulfuric acid and subsequent separation of the chromium sulfate precipitate [4]; and 2) the dissolving of freshly prepared chromium hydroxide in a mixture of nitric and sulfuric acids and precipitation of the resulting chromium sulfate with alcohol [4].

Due to the small yield of product (up to 65%), the great cost and cumbersome nature (second method), these methods can have only laboratory significance.

Chromium sulfate in solution can be conveniently obtained from chromic anhydride by the method of reducing the latter with sulfur dioxide to the stage of forming $Cr_2(SO_4)_3$. The excess dissolved sulfur dioxide is removed by boiling the solution. Here the latter shows a green color. To obtain the solid neutral chromium sulfate from such a solution is difficult, since here basic salts are usually formed.

It seemed of interest to study the possibility of obtaining the chromium sulfate from a strongly acid medium, in order to avoid its hydrolysis during crystallization.

For this we utilized the double decomposition reaction of chromium nitrate with sulfuric acid, based on the difference in the solubility of chromium nitrate and chromium sulfate. It is an easy matter to obtain a sufficiently pure chromium nitrate.

EXPERIMENTAL

A known weight of chromium nitrate (usually the hexahydrate) is dissolved at room temperature in the minimum amount of water (saturated solution). The sulfuric acid solution (1:1) is prepared in a second flask, in an amount showing stoichiometric agreement with the equation:

$$2Cr(NO_3)_3 + 3H_2SO_4 + nH_2O \rightarrow Cr_2(SO_4)_3 \cdot nH_2O + 6HNO_3.$$

The flask containing the chromium nitrate solution is placed in a cooling mixture composed of ice and salt. The sulfuric acid solution (also previously cooled) is slowly added to this solution with stirring of the latter. Here a copious precipitate of chromium sulfate is formed. The latter is suction-filtered on a porcelain funnel.

The adsorbed nitric acid can be removed either by evaporation in vacuo or by blowing warm air over the chromium sulfate preparation (the temperature of the air should not exceed 50°, as otherwise partial dehydration will take place). In the preparation of small amounts of chromium sulfate, the nitric acid can be removed by washing the chromium sulfate precipitate with alcohol, followed by suction-filtration of the liquid phase. The product yield is close to the theoretical.

The chromium sulfate obtained by the described method appears as tiny leaflets with a lilac color and showing good solubility in water. When a solution of the obtained preparation was tested for precipitation of the sulfate ion with benzidine hydrochloride it was revealed that about 1/3 (30.7%) of the total sulfate ions fail to be precipitated by the benzidine, and consequently they are coordinately linked.

Found %: Cr 15.51; SO_4 43.37; H_2O 41.3. $Cr_2(SO_4)_3 \cdot 15H_2O$. Calculated %: Cr 15.71; SO_4 43.52; H_2O 40.77.

To characterize the preparation obtained by us it seemed desirable to make a thermographic study of the latter. There is very little information in the literature relative to the processes that prevail when the crystallohydrates of chromium sulfate are heated. The existing studies have been devoted for the most part to a study of dehydration. Thus, Hackspill and Kieffer [5] studied the dehydration (by the heating method) of differently prepared chromium sulfate hexahydrates. The results obtained by them are shown in Fig. 1, where Curve I characterizes dehydration of the hexahydrate that was obtained by the regime of keeping the violet form of chromium sulfate at 100° for 5 hours until it was transformed into the hexahydrate, and Curve II represents dehydration of the chromium sulfate hexahydrate that was obtained from solution by the Recoura method [6], i.e. by the reduction of chromic acid with alcohol. The solution of the last preparation failed to give a test for sulfate ion when reacted with barium chloride, i.e. all three SO_4-groups were found in the inner sphere of the complex.

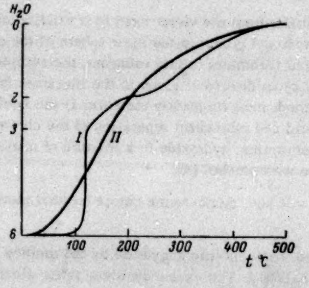

Fig. 1. Dehydration curves of chromium sulfate hexahydrate samples prepared by different methods.

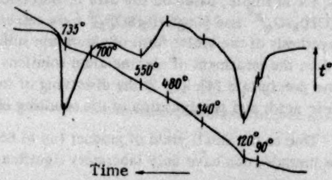

Fig. 2. Thermogram of chromium sulfate with composition $Cr_2(SO_4)_3 \cdot 15H_2O$.

The above-mentioned authors [5] stated that chromium sulfate samples prepared by various methods (but containing the same number of moles of crystallization water) showed different dehydration processes, but they failed to give an explanation of this phenomenon.

Data is also available in the literature [7] on the dissociation pressure shown by basic chromium sulfate when it is heated.

The difference in behaviour shown by various chromium sulfate samples, all containing the same number of moles of water, when subjected to thermal dehydration should apparently be explained as being due to a difference in the bonding character of the water and SO_4-groups with chromium, which is reflected on the curves of the phase transformations during heating.

We made a thermographic study of the obtained preparation $Cr_2(SO_4)_3 \cdot 15H_2O$ in the temperature range of 18 to 800°. The thermogram was taken on a N. S. Kurnakov automatic pyrometer by the differential recording method with a heating rate of 6°/min. in an open crucible. Magnesium oxide was taken as a standard.

To decipher the thermal effects on the thermogram we made a study of the weight loss when the substance was heated in an open crucible and observed the changes that took place here. In addition, we analyzed the thermal decomposition products after heating the preparation at 200 and 400°. The results of this study revealed the following.

Heating of the substance to 50° fails to result in any changes. Heating to 90-95° leads to the substance turning completely green (through the whole mass) without changing the crystal form. Here the crystallohydrate loses 6 moles of water, being converted to the 9-hydrate, and the heat effect is recorded on the thermogram. Further heating to 120° leads to the loss of another 3 moles of water and the substance is transformed into the hexahydrate. This last transformation is accompanied by a large heat effect, as can be seen from the thermogram (Fig. 2). Further on the differential curve there is a sharp rise, accompanied by the removal of part of the water. At 340° a new endothermic effect is observed, accompanied by a change in the crystal color from green to gray (graphitic). At 480° an exothermic effect is recorded. The substance turns from a gray (graphitic) to an olive color, and water is completely absent. At 550° an endothermic effect is observed and the substance assumes a friable amorphous appearance. At 700° the chromium sulfate begins to decompose to the oxide and at 735° the decomposition is accompanied by a profound endothermic effect, which corresponds to the complete decomposition of the chromium sulfate to Cr_2O_3 and SO_3. The final product from the heating is a green powder, which fails to show noticeable solution even in hot aqua regia.

It seemed of interest to establish whether the process for dehydration of the chromium sulfate hexahydrate is accompanied by the formation of basic salts (due to possible hydrolysis or else the latter fails to occur here). In connection with this we analyzed, as already mentioned above, selected samples of the products obtained under heating at 200 and 400°. The results revealed that hydrolysis is absent when the dehydration is run under our experimental conditions, which is supported by the chemical analysis data obtained for the products of heating, showing a ratio of chromium to sulfate-ion equal to 1:1.49 and 1:1.50 at 200 and 400°, respectively, in which connection the weight loss at 400° was 40.3%, which corresponds to practically complete removal of all of the water contained in the chromium sulfate crystallohydrate.

The results obtained by us are evidence that it is impossible to identify the processes, determining the color (either violet or green) of chromium sulfate as a solid, with the processes that prevail in solutions, where the appearance of a green color is associated (among other reasons) with the presence of hydroxyl groups in the inner sphere of the complex.

SUMMARY

1. A method for the preparation of chromium sulfate was described, being based on the double decomposition reaction of chromium nitrate with sulfuric acid.

2. A thermographic study of the chromium sulfate crystallohydrate having the composition $Cr_2(SO_4)_3 \cdot 15H_2O$ was made in the temperature range from 18 to 800°. Here it was established that the dehydration process takes place without hydrolysis of the chromium sulfate. The decomposition of chromium sulfate to the oxide is complete at 735°.

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Received May 30, 1955

Institute of General and Inorganic
Chemistry of the Academy of Sciences
of the Ukrainian SSR

HETEROGENEOUS EQUILIBRIA IN AQUEOUS TERNARY SYSTEMS OF BERYLLIUM CHLORIDE WITH THE CHLORIDES OF FIRST GROUP METALS

V. P. Blidin

Beryllium, being first in the second group of the periodic system, in its physicochemical properties differs from the members of both the first and second groups. The chief beryllium-containing mineral is beryl – the beryllium-aluminum silicate $Be_3Al_2(SiO_3)_6$, having a theoretical beryllium content of 5.1%. Li_2O, Na_2O, K_2O, Rb_2O and Cs_2O are frequently present as impurities [1]. These facts indicate that a study of the behavior of beryllium compounds in the presence of compounds derived from the metals of the first and second groups is of undoubted interest.

A number of authors [2,3] have studied the system $LiCl - BeCl_2 - H_2O$. The salting out of LiCl by beryllium chloride was observed in this system. The presence of chemical compounds and solid solutions was not revealed.

EXPERIMENTAL

As starting substances we took c.p. salts that had been recrystallized twice. Chlorine was determined gravimetrically. Beryllium was precipitated as the hydroxide with dilute ammonia solution. The obtained hydroxide was dried and then ignited to constant BeO weight. Potassium was determined as potassium-sodium cobaltinitrite. Copper was determined iodometrically. In each system the chloride ion and one of the cations were determined quantitatively, while the other cation was calculated by difference from the total amount of chlorides.

The solubilities of the systems were studied in a water thermostat. A temperature of 25° was maintained with an accuracy of ± 0.1°. The solution with excess solid phase was placed in a reaction vessel with an oil seal and stirred until equilbrium between the liquid and solid phases had been achieved. The composition of the solid phases was established by the Schreinemakers method of "residues". The obtained data permitted constructing the solubility isotherms at 25° for each system.

In the plots of the equilibria on the diagrams the composition are expressed in weight percents.

Isotherm of the System $BeCl_2$ - NaCl - H_2O (Table 1, Fig. 1). Based on the data in Table 1 it can be seen that in measure with saturating the solution with beryllium chloride the NaCl solubility shows a sharp decrease, i.e. salting out is observed. The branch for the crystallization of NaCl occupies the whole isotherm. This appears as a criterion for those systems in whose aqueous solutions one of the components plays the role of a powerful salting-out agent with respect to the other. A $BeCl_2$ branch was not found.

Isotherm of the System $BeCl_2$ - KCl - H_2O (Table 2, Fig. 2). As in the previous case, the isothermal section of the diagram of state for the system $BeCl_2$ - KCl - H_2O shows only one branch, corresponding to the crystallization of KCl. The straight lines, connecting the figurative points of the saturated solutions, and the points depicting the composition of the system, pass through the KCl apex.

Isotherm of the System $BeCl_2$ - RbCl - H_2O (Table 3, Fig. 3). In studying the given system, and also the system $BeCl_2$ - CsCl - H_2O, it was revealed that in measure with adding increasing amounts of either

TABLE 1

Amount of salts in unsaturated solutions (in wt. %)		Composition of the solid phase (in wt. %)		Solid phase
NaCl	BeCl$_2$	NaCl	BeCl$_2$	
26.50	—	—	—	NaCl
21.37	3.74	59.67	1.69	
15.64	7.86	61.97	3.18	
12.42	10.29	56.79	5.16	
8.15	14.28	56.44	6.88	
4.09	18.49	54.78	8.69	
2.96	19.87	59.85	8.09	
1.75	22.52	45.29	12.62	
1.05	25.84	42.53	15.15	
—	28.85	45.11	16.68	
—	41.72	—	—	$BeCl_2 \cdot 4H_2O$

TABLE 2

Amount of salt in saturated solutions (in wt. %)		Composition of the solid phase (in wt. %)		Solid phase
KCl	BeCl$_2$	KCl	BeCl$_2$	
26.48	—	—	—	KCl
24.24	1.44	72.11	0.50	
14.05	9.60	70.20	4.13	
18.11	5.52	70.24	2.22	
8.92	13.02	70.50	3.94	
6.01	17.99	68.77	5.83	
3.65	23.93	65.80	8.84	
2.73	32.22	63.43	12.34	
0.80	34.30	56.58	14.79	
—	41.72	—	—	$BeCl_2 \cdot 4H_2O$

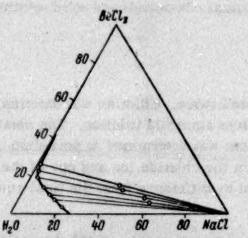

Fig. 1. Solubility isotherm at 25° of the system $BeCl_2$ - NaCl - H_2O.

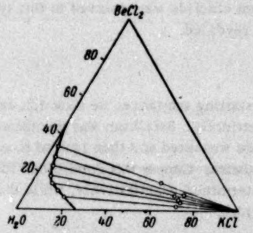

Fig. 2. Solubility isotherm at 25° of the system $BeCl_2$ - KCl - H_2O.

RbCl or CsCl to a saturated $BeCl_2$ solution the viscosity of the solution increased up to the limiting concentrations of the added components. Two isotherms were obtained on the diagram: Branch AB corresponds to the crystallization of $BeCl_2 \cdot 4H_2O$ and BC corresponds to the crystallization of RbCl. The eutonic point (B), derived by interpolation, corresponds to the composition 37.14% $BeCl_2$ and 5.16% RbCl.

Isotherm of the System $BeCl_2$ - CsCl - H_2O (Table 4, Fig. 4). The isothermal section of the diagram of state for this system is comparable to the preceding: Branch AB corresponds to the crystallization of $BeCl_2 \cdot 4H_2O$ and BC corresponds to the crystallization of CsCl. The univariant equilibrium of the solution with the solid phases (point B) $BeCl_2 \cdot 4H_2O$ and CsCl corresponds to the composition 37.50% $BeCl_2$ and 13.38% CsCl. The system differs from the preceding by a longer extension of the beryllium chloride tetrahydrate crystallization branch.

This is explained not only by the greater solubility of CsCl, but also by its tendency to form unstable complexes in the given system. Proof of the latter is the fact that in measure with adding CsCl to a saturated $BeCl_2$ solution there is noticeable transition of the solid phase into solution. We had observed a similar phenomenon in the system LiCl - CsCl - H_2O [4].

TABLE 3

Amount of salts in saturated solutions (in wt. %)		Composition of the solid phase (in wt. %)		Solid phase
$BeCl_2$	RbCl	$BeCl_2$	RbCl	
41.72	—	—	—	$BeCl_2 \cdot 4H_2O$
39.37	2.45	46.30	1.52	
37.14	5.16	—	—	$BeCl_2 \cdot 4H_2O + RbCl$
34.70	8.60	9.37	74.16	RbCl
30.48	12.03	9.13	75.08	
27.60	14.22	7.40	76.20	
23.16	18.25	6.27	77.43	
20.18	21.40	5.38	78.50	
15.10	26.54	4.90	77.11	
8.94	34.13	1.54	81.46	
4.80	39.76	1.92	80.15	
2.51	42.60	0.86	84.51	
—	48.12	—	—	

TABLE 4

Amount of salts in saturated solutions (in wt. %)		Composition of the solid phase (in wt. %)		Solid phase
$BeCl_2$	CsCl	$BeCl_2$	CsCl	
41.72	—	—	—	$BeCl_2 \cdot 4H_2O$
39.46	4.50	43.12	2.60	
38.60	9.24	42.70	5.15	
37.50	13.38	—	—	$BeCl_2 \cdot 4H_2O + CsCl$
34.40	16.62	8.61	81.10	CsCl
29.88	21.37	7.22	80.90	
23.75	30.10	5.10	84.17	
19.64	34.65	4.15	84.82	
14.25	42.36	3.12	85.44	
10.41	45.20	3.08	85.66	
5.48	54.12	1.46	86.56	
2.10	61.83	1.30	87.47	
—	65.51	—	—	

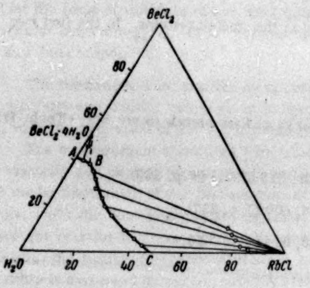

Fig. 3. Solubility isotherm at 25° of the system $BeCl_2$ - RbCl - H_2O.

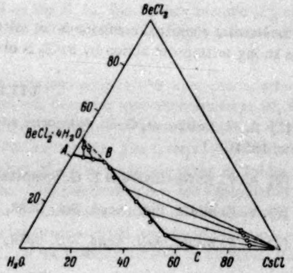

Fig. 4. Solubility isotherm at 25° of the system $BeCl_2$ - CsCl - H_2O.

TABLE 5

Amount of salts in saturated solutions (in wt. %)		Composition of the solid phase (in wt. %)		Solid phase
$BeCl_2$	$CuCl_2$	$BeCl_2$	$CuCl_2$	
41.72	—	—	—	$BeCl_2 \cdot 4H_2O$
40.60	1.10	45.10	1.28	
39.18	2.45	—	—	$BeCl_2 \cdot 4H_2O + CuCl_2 \cdot 2H_2O$
37.50	4.20	15.12	49.42	$CuCl_2 \cdot 2H_2O$
31.87	6.66	11.80	52.50	
29.20	8.27	10.40	54.13	
25.10	10.60	9.12	54.48	
20.12	14.46	9.14	55.30	
18.20	16.25	7.06	56.24	
14.66	20.12	5.75	57.16	
11.70	24.36	4.16	57.40	
6.87	31.50	2.48	62.18	
2.20	39.62	1.27	64.10	
—	44.62	—	—	

Isotherm of the System $BeCl_2$ - $CuCl_2$ - H_2O (Table 5, Fig. 5). Based on the data in Table 5 we constructed the isothermal section of the diagram of state, in which two isotherms are present: the short Branch AB corresponds to the crystallization of $BeCl_2 \cdot 4H_2O$, while Branch BC corresponds to the crystallization of $CuCl_2 \cdot 2H_2O$. We were unable to show the presence of either chemical compounds or solid solutions in the system, despite the fact that in general copper compounds show a tendency for complex-formation. Point B at the intersection of the isotherms is a eutonic point. It corresponds to a univariant equilibrium of the solution with the solid phases $BeCl_2 \cdot 4H_2O$ and $CuCl_2 \cdot 2H_2O$ and corresponds to the composition 39.18% $BeCl_2$ and 2.45% $CuCl_2$.

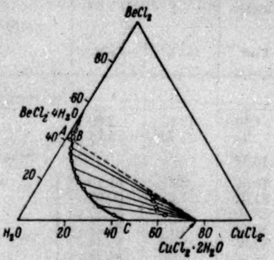

Fig. 5. Solubility isotherm at 25° of the system $BeCl_2$ - $CuCl_2$ - H_2O.

SUMMARY

1. The isothermal method (at 25°) was used to study the systems: $BeCl_2$ - NaCl - H_2O, $BeCl_2$ - KCl - H_2O, $BeCl_2$ - RbCl - H_2O, $BeCl_2$ - CsCl - H_2O and $BeCl_2$ - $CuCl_2$ - H_2O.

2. Neither chemical compounds nor solid solutions were found in the studied systems. In the first two systems strong salting-out action by $BeCl_2$ is observed.

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Received June 2, 1955

Rostov-on-Don Institute
of Agricultural Machinery Construction

VISCOSITY, DENSITY AND MOLECULAR BOND ENERGIES OF SOME BINARY SYSTEMS

A. P. Toropov

Here we present the data on the viscosity and density of a number of binary systems, the components of which belong to the same class of chemical compounds (acetone-methyl ethyl ketone, acetone-methyl propyl ketone, methyl ethyl ketone-methyl propyl ketone, n-propyl acetate-n-butyl acetate, isoamyl acetate-n-butyl acetate, isopropyl alcohol-isobutyl alcohol, n-butyl alcohol-isobutyl alcohol, isoamyl alcohol-isobutyl alcohol), and on the basis of this data the values (in cal./ mole), calculated by the G. M. Panchenkov method [1], of the molecular bond energy ϵ_{C}. of the components in the mixture and the molecular bond energy ϵ_{12} between the 1st and 2nd components.

The substances were purified by conventional methods. The obtained preparations were characterized by the viscosity and density values given in the tables. The viscosities and densities were determined at 20, 40 and 60°, with the exception of the two systems containing acetone, where the measurements were made at 20 and 40°. The measurement conditions were analogous to those described earlier [2]. The interpolated results of the viscosity and density measurements and also the calculated values of $\epsilon_{C.}$ and ϵ_{12}, are given in Tables 1-8. The molar fractions N of the first component are shown in the table. The viscosity values are expressed in millipoises, while the bond energies are expressed in calories per mole. In the systems formed by ketones and by esters the relationship between the bond energy of the mixture and the composition, expressed in mole fractions, is, within the limits of experimental error, a straight line function. In the systems, formed by alcohols, this relationship is expressed by curves, strongly convex to the composition axis.

TABLE 1

System Methyl Ethyl Ketone-Acetone

N	20°		40°		$\epsilon_{c.}$	ϵ_{12}
	η	d_4^{20}	η	d_4^{40}		
0.0	3.18	0.7903	2.66	0.7666	1423	—
0.2	3.34	0.7936	2.78	0.7706	1470	1539
0.4	3.50	0.7967	2.90	0.7744	1538	1580
0.6	3.65	0.7994	3.02	0.7778	1580	1564
0.8	3.81	0.8021	3.14	0.7810	1619	1539
1.0	3.97	0.8046	3.26	0.7840	1671	—

TABLE 2

System Methyl Propyl Ketone-Acetone

N	20°		40°		$\epsilon_{c.}$	ϵ_{12}
	η	d_4^{20}	η	d_4^{40}		
0.0	3.18	0.7903	2.66	0.7666	1423	—
0.2	3.55	0.7953	2.94	0.7727	1538	1714
0.4	3.91	0.7998	3.22	0.7781	1657	1728
0.6	4.29	0.8036	3.49	0.7828	1754	1702
0.8	4.67	0.8069	3.77	0.7870	1871	1729
1.0	5.06	0.8097	4.05	0.7903	1970	—

It is interesting to compare the data obtained by us for the relationship between the molecular bond energies and the composition (in mole fractions) with those given in the literature. In the systems formed by

TABLE 3

System Methyl Ethyl Ketone-Methyl Propyl Ketone

N	20°		40°		60°		E_a.	E_{12}
	η	d_4^{20}	η	d_4^{40}	η	d_4^{60}		
0.0	5.06	0.8097	4.05	0.7903	3.32	0.7705	1970	—
0.2	4.83	0.8089	3.88	0.7891	3.20	0.7692	1911	1823
0.4	4.61	0.8079	3.72	0.7880	3.09	0.7676	1850	1820
0.6	4.39	0.8069	3.57	0.7868	2.97	0.7661	1795	1830
0.8	4.18	0.8058	3.41	0.7854	2.86	0.7644	1727	1808
1.0	3.97	0.8046	3.26	0.7840	2.75	0.7625	1671	—

TABLE 4

System n-Propyl Acetate-n-Butyl Acetate

N	20°		40°		60°		E_a.	E_{12}
	η	d_4^{20}	η	d_4^{40}	η	d_4^{60}		
0.0	7.24	0.8809	5.56	0.8599	4.42	0.8388	2328	—
0.2	6.97	0.8815	5.38	0.8603	4.28	0.8389	2296	2253
0.4	6.70	0.8821	5.19	0.8607	4.14	0.8389	2256	2244
0.6	6.44	0.8828	5.00	0.8612	4.00	0.8390	2220	2251
0.8	6.18	0.8834	4.81	0.8616	3.87	0.8390	2176	2247
1.0	5.91	0.8840	4.62	0.8620	3.73	0.8391	2131	—

TABLE 5

System Isoamyl Acetate-n-Butyl Acetate

N	20°		40°		60°		E_a.	E_{12}
	η	d_4^{20}	η	d_4^{40}	η	d_4^{60}		
0.0	7.24	0.8809	5.56	0.8599	4.42	0.8388	2328	—
0.2	7.50	0.8789	5.75	0.8585	4.55	0.8377	2366	2421
0.4	7.76	0.8771	5.92	0.8572	4.68	0.8366	2402	2414
0.6	8.02	0.8755	6.11	0.8558	4.81	0.8355	2440	2408
0.8	8.31	0.8747	6.29	0.8545	4.94	0.8344	2482	2399
1.0	8.60	0.8731	6.49	0.8533	5.06	0.8333	2533	—

aliphatic hydrocarbons (n-heptane-n-octane, n-heptane-2,2,4-trimethylpentane, n-octane-2,2,4-trimethylpentane) [2] this relationship is linear,. In the systems formed by armoatic hydrocarbons [3] the examined relationship is depicted by straight lines (toluene-o-xylene, toluene-cumene), by curves that are convex to the composition axis (benzene-toluene), and in most of the studied systems, by curves that pass through a minimum

TABLE 6

System Isopropyl Alcohol-Isobutyl Alcohol

N	20°		40°		60°		ε_0.	ε_{12}
	η	d_4^{20}	η	d_4^{40}	η	d_4^{60}		
0.0	40.09	0.8016	21.38	0.7862	12.33	0.7696	5757	—
0.2	35.36	0.7993	19.23	0.7834	12.20	0.7664	5605	5338
0.4	31.63	0.7963	17.42	0.7802	10.29	0.7627	5469	5306
0.6	28.56	0.7929	15.86	0.7766	9.40	0.7587	5407	5362
0.8	25.97	0.7896	14.49	0.7728	8.67	0.7545	5329	5311
1.0	23.85	0.7855	13.34	0.7684	7.98	0.7497	5311	—

TABLE 7

System n-Butyl Alcohol-Isobutyl Alcohol

N	20°		40°		60°		ε_0.	ε_{12}
	η	d_4^{20}	η	d_4^{40}	η	d_4^{60}		
0.0	40.09	0.8016	21.38	0.7862	12.33	0.7696	5757	—
0.2	36.80	0.8039	20.22	0.7833	11.92	0.7717	5502	5080
0.4	34.34	0.8056	19.37	0.7900	11.67	0.7736	5274	5102
0.6	32.43	0.8071	18.72	0.7915	11.47	0.7752	5082	5140
0.8	30.78	0.8084	18.18	0.7930	11.32	0.7767	4893	5163
1.0	29.39	0.8096	17.66	0.7941	11.25	0.7783	4704	—

TABLE 8

System Isoamyl Alcohol-Isobutyl Alcohol

N	20°		40°		60°		ε_0.	ε_{12}
	η	d_4^{20}	η	d_4^{40}	η	d_4^{60}		
0.0	40.09	0.8016	21.38	0.7862	12.33	0.7696	5757	—
0.2	40.48	0.8038	21.78	0.7885	12.68	0.7721	5671	5522
0.4	40.99	0.8056	22.20	0.7904	13.05	0.7742	5595	5508
0.6	41.63	0.8070	22.70	0.7919	13.43	0.7759	5534	5491
0.8	42.41	0.8080	23.26	0.7931	13.82	0.7772	5489	5449
1.0	43.66	0.8086	23.92	0.7938	14.23	0.7781	5492	—

(benzene-cumene, benzene-o-xylene, benzene-p-xylene, benzene-ethylbenzene, toluene-p-xylene, toluene-ethylbenzene). From a comparison of the existing data it follows that the relationship between molecular bond energies and composition (in mole fractions) in systems devoid of chemical reaction between components can be expressed not only by curves, convex to the composition axis, as R. P. Airapetova and R. I. Filatova [4] indicate, but also by curves with a minimum, and also by straight lines.

SUMMARY

1. We studied the viscosity and density of the systems methyl ethyl ketone-acetone and methyl propyl ketone-acetone (at 20 and 40°), and of methyl ethyl ketone-methyl propyl ketone, n-propyl acetate-n-butyl acetate, isoamyl acetate-n-butyl acetate, isopropyl alcohol-isobutyl alcohol, n-butyl alcohol-isobutyl alcohol and isoamyl alcohol-isobutyl alcohol (at 20, 40 and 60°).

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Received March 10, 1955

Central Asia State University

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* T.p. = C. B. Translation pagination.

IRREVERSIBLE-RECIPROCAL SYSTEM OF SODIUM AND CADMIUM CHLORIDES AND IODIDES

I. I. Ilyasov and A. G. Bergman

Of the reciprocal systems composed of the chlorides and iodides of cadmium and univalent metals this system is the simplest, since here the compounds $CdCl_2 \cdot 2NaCl$ and our established $CdI_2 \cdot 2NaI$, both melting with decomposition, are formed on the two opposite sides.

The conditional heat effect of the exchange reaction is equal to 6.7 kcal./ equiv.

$$\begin{array}{lcl} \underset{138.56}{2NaI} + \underset{93.1}{CdCl_2} & \rightarrow & \underset{196.66}{2NaCl} + \underset{48.40}{CdI_2} \end{array}$$

The system was studied by the visual-polythermal method; all of the compositions are expressed in equivalent percents.

Binary Systems

1. Na_2Cl_2 - Na_2I_2 was studied by M. Amadori [1,2]. The eutectic point lies at 578° and 36% Na_2Cl_2. Limited solid solutions exist in the interval of 0-24% NaCl and solid solutions on the Na_2Cl_2 side (the exact concentration is not indicated). From our data the eutectic corresponds to 585° and 37.5% Na_2Cl_2 (Fig. 1, Table 1).

2. $CdCl_2$ - CdI_2 was studied by E. Nacken [3]; the eutectic point lies at 359° and 30% $CdCl_2$. Limited solid solutions exist in the intervals 0-2% and 96-100% $CdCl_2$. From our data the eutectic corresponds to 359° and 31% $CdCl_2$ (Fig. 1, Table 1).

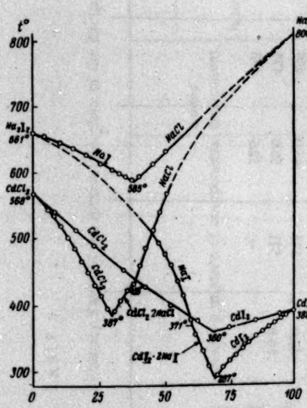


Fig. 1. Binary systems.

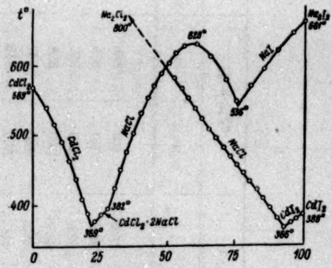


Fig. 2. Diagonal systems.

3. Na_2Cl_2 - $CdCl_2$ was studied by Brand [4]; a eutectic was revealed at 392° and 29% Na_2Cl_2, and a transition point at 423° and 39.8% Na_2Cl_2. We repeated a study of the system. The fusion curve consists of three branches: $CdCl_2$, $CdCl_2 \cdot 2NaCl$ and Na_2Cl_2.

TABLE 1

$CdCl_2$—Na_2Cl_2		CdI_2—Na_2I_2		$CdCl_2$—CdI_2		Na_2I_2—Na_2Cl_2	
% Na_2Cl_2	t	% Na_2I_2	t	% $CdCl_2$	t	% Na_2Cl_2	t
0.0	569°	0.0	388°	0.0	388°	0.0	661°
5.0	549	5.0	375	5.0	383	10.0	646
10.0	522	10.0	363	14.0	376	15.0	638
15.0	485	15.0	351	25.4	365	20.0	626
20.0	450	20.0	332	37.1	375	25.0	613
25.0	415	25.0	313	48.0	399	30.0	602
27.5	395	27.5	306	57.5	429	32.5	599
30.0	391	30.0	292	65.4	452	35.0	592
32.5	408	32.5	306	72.0	472	37.5	587
35.0	423	35.0	328	77.1	490	40.0	592
37.5	434	37.5	354	83.9	513	45.0	611
40.0	460	40.0	386	94.7	544	50.0	631
45.0	514	45.0	435	100.0	568	—	—
50 0	571	50.0	474	—	—	—	—
—	—	52.5	492	—	—	—	—

TABLE 2

Diagonal $CdCl_2$—Na_2I_2		Diagonal CdI_2—Na_2Cl_2	
% Na_2I_2	t	% Na_2Cl_2	t
0.0	568°	0.0	388°
5.0	538	2.5	379
10.0	489	5.0	374
15.0	437	7.5	367
20.0	386	10.5	380
22.5	373	12.5	392
25.0	386	15.0	408
27.5	391	17.5	420
30.0	420	20.0	434
35.0	478	22.5	446
45.0	568	25.0	456
50.0	600	27.5	468
55.0	625	30.0	480
60.0	627	32.5	492
65.0	612	35.0	507
70.0	575	37.5	521
75.0	540	40.0	536
80.0	568	42.5	550
90.0	620	45.0	567
		47.5	580

TABLE 3

Summary Table of the Internal Sections of the Reciprocal System Na, Cd ‖ Cl, I

Section nos.	Starting mixture of components	Added component	Branches of the crystallization curves and their intersections									
			branch 1	intersection of 1 and 2		branch 2	intersection of 2 and 3		branch 3	intersection of 3 and 4		branch 4
				%	melting point		%	melting point		%	melting point	
I	90% $CdCl_2$+10% CdI_2	Na_2I_2	$CdCl_2$	19.0	360°	$CdCl_2 \cdot 2NaCl$	25.0	385°	Na_2Cl_2	76.5	528°	Na_2I_2
II	90% $CdCl_2$+10% CdI_2	Na_2Cl_2	$CdCl_2$	25.0	381	$CdCl_2 \cdot 2NaCl$	34.5	417	Na_2Cl_2			
III	80% $CdCl_2$+20% CdI_2	Na_2Cl_2	$CdCl_2$	23.5	375	$CdCl_2 \cdot 2NaCl$	32.5	410	Na_2Cl_2			
IV	65% $CdCl_2$+35% CdI_2	Na_2I_2	$CdCl_2$	13.0	351	$CdCl_2 \cdot 2NaCl$	17.5	383	Na_2Cl_2			
V	50% $CdCl_2$+50% CdI_2	Na_2I_2	$CdCl_2$	7.5	350	$CdCl_2 \cdot 2NaCl$	12.5	382	Na_2Cl_2	61.0	497	Na_2I_2
VI	47.5% $CdCl_2$+52.5% CdI_2	Na_2I_2	$CdCl_2$	8.0	347	$CdCl_2 \cdot 2NaCl$	11.0	365	Na_2Cl_2			
VII	45.0% $CdCl_2$+55% CdI_2	Na_2I_2	$CdCl_2$	7.0	347	Na_2Cl_2						
VIII	35% $CdCl_2$+65% CdI_2	Na_2I_2	$CdCl_2$	6.5	344	Na_2Cl_2	63.5	469	Na_2I_2			
IX	20% $CdCl_2$+80% CdI_2	Na_2Cl_2	CdI_2	5.0	354	Na_2I_2						
X	10% $CdCl_2$+90% CdI_2	Na_2I_2	CdI_2	5.0	364	Na_2Cl_2	43.0	380	Na_2I_2			
XI	2.5% $CdCl_2$+97.5% CdI_2	Na_2I_2	CdI_2	31.0	285	$CdI_2 \cdot 2NaI$	38.5	355	Na_2I_2			
XII	15% Na_2I_2 +85% CdI_2	$CdCl_2$	CdI_2	5.0	352	Na_2Cl_2						
XIII	25.0% Na_2I_2 +75% CdI_2	$CdCl_2$	CdI_2	4.0	314	Na_2Cl_2						
XIV	35% Na_2I_2 +65% CdI_2	$CdCl_2$	$CdI_2 \cdot 2NaI$	4.0	306	Na_2Cl_2						
XV	85% Na_2I_2 +15% CdI_2	Na_2Cl_2	Na_2I_2	32.5	562	Na_2Cl_2						

TABLE 4

Section IV		Section V		Section VI		Section VII		Section VIII		Section IX		Section XIII		Section XIV	
% Na_2I_2	t	% Na_2I_2	t	% Na_2I_2	t	% Na_2I_2	t	% Na_2I_2	t	% Na_2Cl_2	t	% $CdCl_2$	t	% $CdCl_2$	t
0.0	456°	0.0	410°	0.0	415°	0.0	396°	0.0	378°	0.0	365°	0.0	314°	0.0	332°
5.0	418	5.0	363	5.0	376	2.5	387	3.0	361	2.0	361	1.0	314	1.0	328
10.0	380	7.5	352	7.0	360	5.0	372	5.0	354	4.0	358	2.0	314	2.0	321
12.5	359	10.0	374	8.0	354	6.0	363	7.5	354	6.0	361	3.0	314	3.0	316
15.0	365	12.5	382	9.0	354	7.0	356	10.0	372	8.0	376	4.0	340	4.0	336
17.5	380	15.0	402	10.0	363	8.0	356	15.0	413	10.0	388	5.0	358	5.0	361
20.0	396	20.0	441	11.0	365	9.0	363	25.0	464	20.0	443	6.0	378	7.0	396
25.0	438	30.0	496	12.5	370	10.0	369	35.0	490	35.0	519	8.0	409	10.0	432
35.0	520	40.0	521	15.0	386	11.0	376	40.0	498	50.0	602	10.0	428	15.0	468
		50.0	533			12.0	382	45.0	501						
		55.0	524			15.0	398	50.0	501						
		60.0	503			17.5	420	55.0	494						
		65.0	527					60.0	481						
		70.0	558					65.0	519						
		80.0	604					70.0	558						

The compound melts with decomposition at 433°; the transition point corresponds to 37.5% Na_2Cl_2. The $CdCl_2 \cdot 2NaCl$ branch intersects the $CdCl_2$ branch in the eutectic point at 387° and 29% Na_2Cl_2 (Fig. 1, Table 1).

4. CdI_2 - Na_2I_2 was studied by Brand [5]; a eutectic was revealed at 287° and 31.5% Na_2I_2. We repeated a study of the system: the fusion curve consists of three branches – CdI_2, Na_2I_2 and our revealed $CdI_2 \cdot 2NaI$, melting with decomposition at 371°. There is a transition point at 39% Na_2I_2. The eutectic point is at 287° and 31.5% Na_2I_2 (Fig. 1, Table 1).

Diagonal and Internal Sections of the System Na, Cd || Cl, I

The Stable Diagonal Section CdI_2 - Na_2Cl_2 (Fig. 2, Table 2) is a triangulating diagonal that intersects the eutectic inversion point at 366° and 7.5% Na_2Cl_2.

The Unstable Diagonal Section CdI_2-Na_2I_2. (Fig. 2, Table 2) intersects fields $CdCl_2$, $CdCl_2 \cdot 2NaCl$ complex, Na_2Cl_2 and Na_2I_2 at 369° and 21.5% Na_2I_2, 382° and 27.5% Na_2I_2, and 536° and 75% Na_2I_2. The maximum at 628° on the Na_2Cl_2 branch is shifted from the plane of the stable diagonal section and corresponds to 57.5% Na_2I_2, which indicates presence of exchange equilibrium in the melts.

Our study results of the internal sections of the system are given in Tables 3 and 4. The plotted data are shown in Figs. 3 and 4.

Surface of Crystallization of the System. By combining the data of the studied binary systems, diagonals and internal sections, and projecting the mutual crystallization lines on the plane of the polytherms of the binary system Na_2I_2 - CdI_2 (Fig. 5), we were able to construct the space diagram for the liquidus of the reciprocal system Cd, Na || Cl, I (Fig. 6,7) and determine the temperatures and compositions corresponding to the invariant points.

The crystallization fields meet in four invariant points: two eutectics E_1 and E_2, one transition and one cross point R (Table 5). The cross point R fails to participate in the triangulation, since in it all three phases of the side binary system are found to be in equilibrium.

The distribution of the area of the composition square among the crystallization fields is given in Table 6.

The diagonal and adiagonal sections of the composition square of the reciprocal system are divided into three phase triangles (Fig. 7):

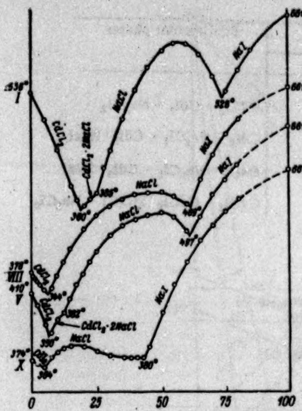


Fig. 3. Sections I, V, VIII and X of the system.

1) $CdCl_2$ - Na_2Cl_2 - CdI_2, 2) Na_2Cl_2 - CdI_2 - $CdI_2 \cdot 2NaI$, 3) Na_2Cl_2 - Na_2I_2 - $CdI_2 \cdot 2NaI$.

The field of the compound $CdCl_2 \cdot 2NaCl$, melting with decomposition, occupies 4.68% of the total area and extends as a deep wedge into the interior of the system. In form it is planar, as is evidenced by the fact that isotherms, drawn through 50°, are absent in it. The field of the compound, $CdI_2 \cdot 2NaI$, also melting with decomposition, occupies a very modest area (0.20%). The crystallization tree of the system is shown in Fig. 8.

SUMMARY

1. The studied reciprocal system Na, Cd ‖ Cl, I is an irreversible-reciprocal system with a stable diagonal section Na_2Cl_2-CdI_2 and a subordinate adiagonal triangulating section Na_2Cl_2- $CdI_2 \cdot 2NaI$; these lines divide the composition square of the reciprocal system into three phase triangles: $CdCl_2$ - Na_2Cl_2 - CdI_2, Na_2Cl_2 - Cd $_2$ - $CdI_2 \cdot 2Na$ and Na_2Cl_2 - Na_2I_2 - $CdI_2 \cdot 2NaI$.

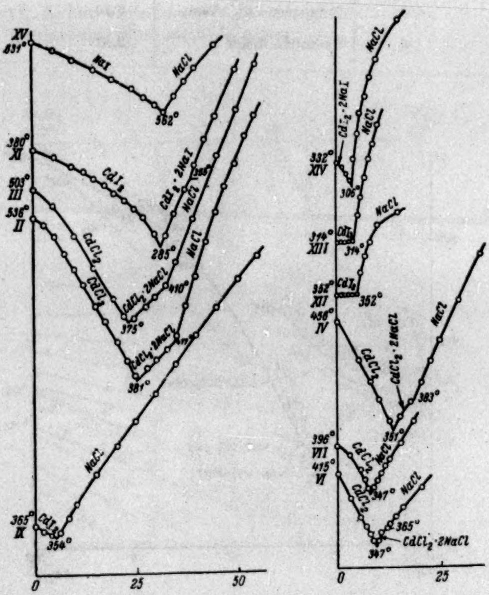


Fig. 4. Sections II, III, IX, XI, XV and IV, VI, VII, XII, XIII, XIV of the system.

TABLE 5

Point	Temperature	Composition (in mole %)				Equilibrium phases
		$CdCl_2$	Na_2Cl_2	CdI_2	Na_2I_2	
E_1	344*	26.0	6.5	67.5	–	$CdCl_2$ - CdI_2 - Na_2Cl_2
E_2	285	–	3.5	70.0	26.5	CdI_2 - Na_2Cl_2 - $CdI_2 \cdot 2NaI$
P	306	–	4.0	65.0	31.0	Na_2I_2 - Na_2Cl_2 - $CdI_2 \cdot 2NaI$
R	347	33.5	7.5	59.0	–	$CdCl_2$ - $CdCl_2 \cdot 2NaCl$ - Na_2Cl_2

TABLE 6

Expt. Nos.	Crystallization field	Area (in %)
1	Sodium chloride	68.60
2	Compound $CdCl_2 \cdot 2NaCl$	4.68
3	Cadmium chloride	10.99
4	Sodium iodide	12.72
5	Compound $CdI_2 \cdot 2NaI$	0.20
6	Cadmium iodide	2.81

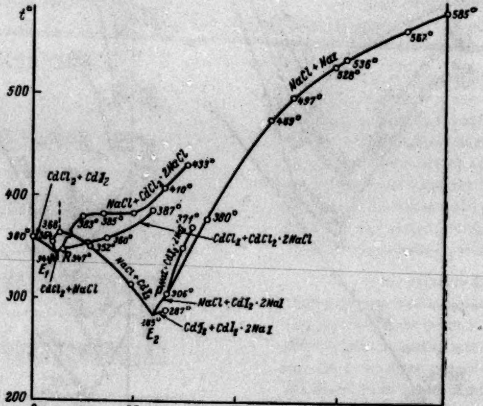
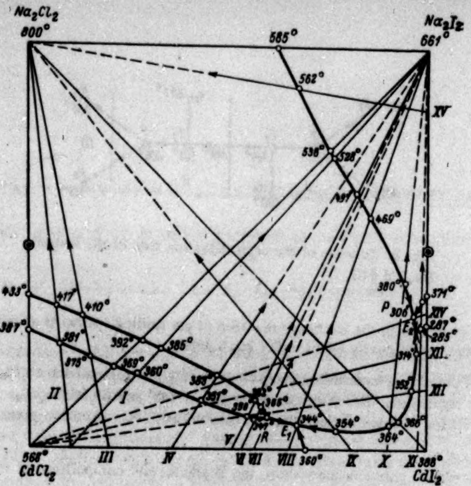
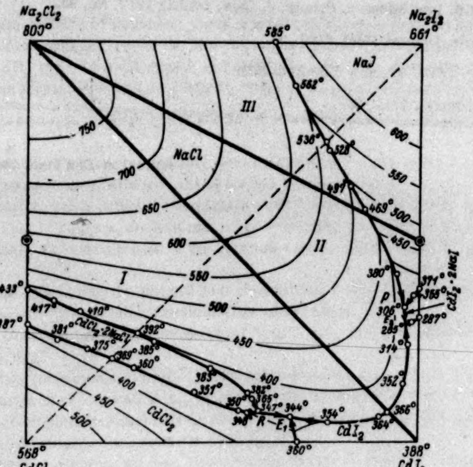


Fig. 5. Projection of the crystallization tree of the reciprocal system on the CdI_2 - Na_2I_2 side.



Na_2Cl_2
800°
Na_2I_2
661°
585°
582°
XV
536°
528°
491°
469°
433°
417°
410°
387°
381°
392°
385°
375°
369°
360°
II
I
383°
351°
350°
365°
346°
347°
R
V
E_1
344°
354°
380°
371°
P
306°
XIV
E_2
287°
285°
314°
XIII
352°
XII
366°
364°
568°
$CdCl_2$
III
IV
VI VII
VIII 360°
IX
X
XI 388°
CdI_2

Fig. 6. Distribution scheme of the sections inside the composition square of the reciprocal system.



Na_2Cl_2
800°
585°
Na_2I_2
661°
NaJ
582°
III
750
NaCl
536°
528°
600
700
550
491°
650
469°
500
450
600
II
580
I
380°
433°
417°
410°
371°
365°
387°
381°
$CdCl_2 \cdot 2NaCl$
392°
306°
287°
285°
$CdI_2 \cdot 2NaI$
375°
369°
385°
360°
500
450
P
E_2
314°
383°
351°
400
352°
400
450
500
$CdCl_2$
350°
385°
365°
347°
344°
346°
R
E_1
354°
CdI_2
366°
364°
360°
568°
$CdCl_2$
388°
CdI_2

Fig. 7. Crystallization surface of the reciprocal system Na, Cd || Cl, I and triangulation of the composition square.

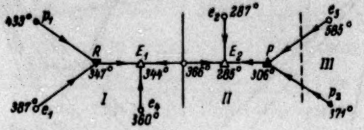


Fig. 8. Scheme of the crystallization tree of the system Na, Cd ‖ Cl, I.

2. The irreversible character of the exchange reaction of our studied system is associated with a positive heat effect for the reaction, conditonally equal to 6.7 kcal./equiv.

3. The existence of the earlier established compound, having the composition $CdCl_2 \cdot 2NaCl$ and melting with decomposition, was confirmed. The transition point lies at 433° and 37.5% Na_2Cl_2. The existence of the compound $CdI_2 \cdot 2NaI$, melting with decomposition, was established. The transition point lies at 371° and 39% Na_2I_2.

4. There are four invariant points in the system, the character and composition of which are shown in Table 5.

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Received June 7, 1955

Rostov-on-Don State University

THERMOCHEMICAL STUDY OF AQUEOUS SOLUTIONS OF ELECTROLYTES

IV.* THERMOCHEMISTRY OF AQUEOUS AMMONIUM CHLORIDE SOLUTIONS

K. P. Mishchenko and A. M. Ponomareva

Earlier [1] we had mentioned that experimental material on the thermochemistry of solutions, that could have found fruitful use in building a theory of solutions, is extremely meager, despite the seeming abundance of handbook data. At the time one of us with coworkers began a systematic study of salt solutions, embracing the region of concentrations ranging from infinite dilution to saturation, and later the studies were conducted at temperatures above standard. The great difficulty of making calorimetric measurements of solution properties (heat capacity, heat of solution, dilution, etc.) and the need for obtaining highly accurate data, dictated by the requirements needed to develop a modern theory of solutions, fully explain the extremely slow accumulation of experimental data on the thermochemistry of solutions. In fact, if 11 salts were described in the indicated paper, for which the integral heats of solution at 25° were measured in the entire concentration range, then at the present time this number can be increased to only 35.** Most of the heat of solution isotherms, given in contemporary thermochemical handbooks [4-6], were obtained by the composers of the tables by combining the data of many investigators, who made their measurements at various temperatures and with variable accuracy.

The polythermal characteristics of individual water-salt systems are even more meager. In 1947 N. K. Voskresenskaya and G. N. Yankovskaya [7] were the first to compare the data existing in the literature on the integral heats of solution (ΔH_m)*** of NaCl, $MgSO_4$ and Na_2SO_4 in water at several temperatures [8-10], supplementing them with their own measurements of ΔH_m $MgSO_4 \cdot 7H_2O$ at 25°, and NaCl and Na_2SO_4 at 50°.

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* Previous papers of this series: K. P. Mishchenko and M. Z. Pronina [1], Yu. Ya. Kaganovich and K. P. Mischenko [2,3].

** We take into consideration only those systems that were studied at 25° in the entire concentration range by one author (excluding the zones of great dilutions, the so-called "debye region").

*** We consider it necessary to again define the designations and meanings of the fundamental values:

ΔH_m – the integral heat of solution, the heat effect accompanying the solution of 1 mole of substance in such an amount of solvent that the concentration of the obtained solution will be equal to m moles of substance in 1000 g of solvent.

ΔH_0 – the initial heat of solution, the integral heat of dissolving 1 mole of substance in an infinitely larger amount of solvent (m = 0). This value is determined by extrapolation.

ΔH_s – the complete heat of solution, the integral heat of dissolving 1 mole of substance with the formation of a saturated solution ($m = m_s$).

$\Delta m_1^{m_2}$ – the intermediate (intermediary) heat of solution, the heat effect accompanying the solution of 1 mole of substance in a solution of concentration m_1, with the formation of a more concentrated solution m_2.

$\Delta H m_2^{m_1}$ – the intermediate (intermediary) heat of dilution, the heat effect accompanying the dilution of a solution containing 1 mole of substance from concentration m_2 to m_1.

ΔH_m^0 – the integral heat of dilution, the heat effect accompanying the dilution of a solution containing 1 mole of substance to infinite dilution (m = 0).

$\Lambda_{2,m}$ – the differential heat of solution, the heat effect observed when 1 mole of substance is added to an infinitely larger amount of solution at constant concentration m. This value is determined either by calculation or graphically.

$\Lambda_{2,s}$ – the final heat of solution, the differential heat of dissolving 1 mole of substance in a saturated solution.

$\Lambda_{1,m}$ – the differential heat of dilution, the heat effect observed when 1 mole of solvent is added to an infinitely larger amount of solution at constant concentration m. This value is determined either by calculation or graphically.

Supplementing the literature data, the paper by Yu. Ya. Kaganovich and K. P. Mishchenko [2] gave the heats of solution for HNO_3 at 40°, KCl at 50°, and $MgSO_4 \cdot 7H_2O$ at 25 and 45° (a limited concentration interval). As a result, even at the present time the combined experimental material of many investigators gives the temperature dependence of heats of solution only for 7 systems.* In examining these data it should again be mentioned that they were obtained at different times by different investigators, using different methods.

Our selection of the system NH_4Cl-H_2O as a study subject was dictated by the following considerations.

At first it was indirectly indicated by Holluta and Werner [11] and by Drucker [12], and then it was mentioned in greater detail in the studies of N. K. Voskresenskaya and K. S. Ponomareva [13] and of Yu. Ya. Kaganovich and K. P. Mishchenko [2,3], that a change in the state of the solvent plays the chief role in changing some thermochemical values as a function of the solution temperature. It was mentioned that in their action on the structure of water different salts can be roughly divided into "stabilizer-salts", the hydrophilic ions of which as the result of forming solvated complexes create structures that are more orderly than that of pure water, and "destroyer-salts", the large and weakly solvated ions of which facilitate break-up of the water structure, failing to be compensated by orderliness in the solvate films. Both types of salts have already been studied [2,7]. It seemed of interest to us to study a system that involved a salt lying intermediate between these two extreme types, and possibly showing small influence on the structure of water. A comparison of a number of physicochemical properties gave basis to assume that the ions NH_4^+ and Cl^- [14,15] should be characterized by small influence on the structure of water.

We measured the integral solution heats of NH_4Cl in water at 25, 50 and 75° in the concentration region of m from 0.01 to 0.04 mole of salt in 1000 g of H_2O to saturation; we verified and corrected the solution heat isotherm at 18°, given in the handbooks [4,5], and we determined the heat capacity of aqueous NH_4Cl solutions at 25, 50 and 75° in the concentration region of 0.2 to 0.3 mole of salt in 1000 g of H_2O to saturation.

The literature data, used by the handbook composers to obtain the integral solution heats of NH_4Cl in water at 18 and 25° [4-6], are few and nonsystematic. Favre and Silbermann [16], Berthelot [17], and Anderson and Noyes [18] give ΔH_m for NH_4Cl without exactly indicating the concentrations of the solutions formed and the measurement temperatures. Colson [19] failed to determine with sufficient accuracy the temperature changes that occurred during experiment; in addition his data relate only to the one concentration m = 0.234 at 14.9 and 22.3°.

Winkelmann [10] measured the solution heat of NH_4Cl in the broad region of m = 0.57 to m = 4.58 moles in 1000 g of H_2O at extremely different temperatures. Interpolation of these values to 25° gives ΔH_m values that show good agreement with those that we obtained by direct measurement at 25°.

Lehtonen [20] determined the solution heat of NH_4Cl in an ice calorimeter (0°), but at the concentrations of 0.0625-0.50 mole in 1000 g of H_2O he failed to detect the exothermal increase characteristic for this region, mention of which was made in the precise studies of Lange and coworkers. Schwartz and Coblans [21], who analyzed Lehtonen's data, express doubt as to their degree of accuracy. In our calculations and comparisons we fail to take into consideration the solution heat isotherm obtained by Lehtonen for NH_4Cl, since in combination with our results it gives anomalies in the temperature coefficients of the solution heats that are both unexplainable and highly improbable. In order to verify the zero isotherm by our method we refrain from either using or interpreting Lehtonen's data.

Mondain-Monval [22] studied the formation heats of solutions in the region of high concentrations close to saturation. The statement made by Mondain-Monval: "Despite the high concentration of the original solution, the salt showed instantaneous solution ...." (p.110), is contradictory to our observations and leads to the thought that his studied solutions were actually still far from saturation. As the initial solution heat, ΔH_0 ("initial heat" by the terminology of Mondain-Monval) was taken as the heat of dissolving 1 mole of salt in 100-400 moles of water, i.e. 0.555-0.14 mole in 1000 g of H_2O (!!). Actually, the integral solution heat for such concentrations is quite different from ΔH_0. The value 3.37 kcal./mole, which the handbook composers [4,5] borrowed from Mondain-Monval as ΔH_m – the integral solution heat of NH_4Cl at m = 5.55 – is actually given by the author as his calculated final solution heat, $\Lambda_{2,s}$, at 0°. However, this is not accurate, since $\Lambda_{2,s}$ should correspond to the concentration of a saturated solution, i.e. m_s = 5.70. A detailed examination of Mondain-Monval's experimental technique and calculations revealed that he assumes a constant error, actually determining not even $\Lambda_{2,s}$, but an intermediate solution heat, ΔH_m^s, for the salt close to saturation. Stackelberg [23] studied the intermediate solution heats and from them, by extrapolating from $m \approx 0,5$ to $m = 0$, he found the initial solution heat $\Delta H_0 = 3930$ cal./ mole at 18°. This value proves to be slightly high. The extrapolation, made by Stackelberg, is fully unjustified, since in the zone of great dilution ($m = 0.3-0.2$ and lower) an increase in heat evolution is observed for all salts. A. S. Fedorov and G. F. Silchenko [24] measured the solution heats of NH_4Cl at 18° for several random concentrations and the dilution heat of the saturated solution. Thomsen [25], Magie [26] and Pratt [27] studied the dilution heats of NH_4Cl solutions. Usually withstanding the test of time, the data of Thomsen in this case when compared with later measurement results proved to insufficiently accurate. The data of Magie are also insufficiently exact; however, they permit the conclusion that the curves of the integral solution heats have a different shape at 22.3 and 3.7°. The same conclusion can be made on the basis of the more exact data of Pratt, relating to the interval 0-33.5°. This is in full agreement with our measurement results. Streeck [28] studied the dilution heats of NH_4Cl solutions practically to infinite dilution at 25°. This work was executed with great accuracy in a Lange differential calorimeter.

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* Data for four salts (NaCl, KCl Na_2SO_4 and $MgSO_4$) have been published [27]; that for NH_4Cl is given in this paper; data for Na_2CO_3 and $MgCl_2$ are found in [7a].

Very few investigators have studied the heat capacity of NH_4Cl solutions: Winkelmann [10] and Marignac [29] determined the mean specific heat capacities in the intervals 3-28°, 17-40° and 20-52° for solutions of several concentrations. Thomsen [30] measured the heat capacities of NH_4Cl at 18° and $m = 0.28-7.40$. The last point on this heat capacity isotherm lies in the region of supersaturated solutions ($m_s = 6.90$). The possibility is not excluded that here NH_4Cl crystals deposited from solution during experiment. It can be specifically for this reason that for Thomsen the heat capacity of the solution $m = 7.40$ proved to be greater at 18° than at 25° (the sum of the heat capacities of water and salt was greater than the heat capacity of the solution).

Faasch [31] also measured the heat capacities of NH_4Cl solutions at 18° and $m = 0.465-3.950$. In Landoldt-Bornstein tables, where Faasch's results are given, a remark is made by the composer that Faasch's data are less accurate than Thomsen's data.

Making use of the above-enumerated heat capacity data, Bichowsky and Rossini [4] recalculated to 18° the ΔH_m of different authors relating to different temperatures and constructed a composite isotherm.

EXPERIMENTAL

To measure the solution heats of NH_4Cl in water and the heat capacities of solutions we used a calorimeter that was fitted with an isothermal shell. The construction principle of such a calorimeter is given in the studies of M. S. Vrevsky [32]. A number of earlier-described [33] modifications were introduced into our calorimetric apparatus. The heat capacity of the calorimeter ("water number") varied, depending on the degree of filling the beaker with liquid and on changing apparatus parts in the limits of 30 to 60 cal./deg., with a total heat capacity for the system of 400 to 570 cal./deg., i.e., it was ~ 10%. The amount of heat, supplied by an electrical heater, was determined from the amperage, voltage drop at the heater and duration of current passage. The temperature changes during experiment were taken with a Beckmann thermometer having 0.01° graduations. In our work the maximum error of the heat capacity determinations was ± 0.3%.

In our work it was revealed that it is expedient to run a calorimetric study of electrolytes in two stages: first to determine the relationship between specific heat capacity and concentration, and then to use the mean interpolated heat capacity values in studying the heats of solution and dilution. Such a method shortens the number of individual experiments and reduces the error of the ΔH_m values.

To obtain the isotherms $\Delta H_m = f(m)$, for the whole concentration range from $m = 0$ to saturation it becomes necessary to combine the direct measurements of the integral solution heats, ΔH_m with the determinations of the intermediate solution heats, $\Delta H_{m_1}^{m_2}$, and of the intermediate dilution heats, $\Delta H_{m_2}^{m_1}$. The maximum experimental error when determining the solution heats was ± 0.4%, and in determining the dilution heats it was ± 0.55%. Actually, since the errors of the separate measurements could show partial compensation, the experimental error always proved to be less than the maximum. The accuracy of the absolute values, obtained in our calorimetric apparatus, was checked by measuring the solution heats and heat capacities of KCl solutions, proposed as being a calorimetric standard [34]. The results obtained at 50 and 75°, where the correction made for the emergent column of the thermometer is less reliable and where the error introduced by evaporation of the solvent acquires greater significance, naturally show a somewhat lower accuracy.

Our method of operation does not permit measuring solution heats in the region of small concentrations (below $m = 0.01$), even when special thermometers with 0.001° graduations are used. In order to determine the

TABLE 1

Integral Solution Heats of NH_4Cl and Specific Heat Capacities of the Solutions at 25°

m $\left(\frac{\text{mole } NH_4Cl}{1000 \text{ g } H_2O}\right)$	0.0299	0.0519	0.1019	0.2016	0.3061	0.3600	0.5023	0.5035	0.6990	0.9981	1.0054	1.3079	1.8404	1.9988	2.2607
C_p (cal./g. deg.)	—	—	—	—	0.981$_4$	—	—	0.967$_2$	—	0.941$_3$	—	—	—	0.895$_5$	—
ΔH_m (cal./mole)	3590	3596	3625	3629	—	3642	3648	—	3634	—	3662	3625*	3655*	—	3640*

m $\left(\frac{\text{mole} NH_4Cl}{1000 \text{ g } H_2O}\right)$	2.3188	2.9003	3.0005	3.5855	3.7963	4.0174	4.7890	5.0025	5.0296	5.5223	6.2251	7.0323	7.0932
C_p (cal./g.deg.)	—	—	0.857$_4$	—	—	—	0.802$_1$	—	—	—	—	0.753$_4$	—
ΔH_m (cal./mole)	3642 *	3650 *	—	3618 *	3608 *	3644 *	—	3587 *	3633 *	3577 *	3585 *	—	3597 **

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* ΔH_m was obtained from the intermediate solution heats.

** ΔH_m was obtained from the dilution heats.

TABLE 2

Integral Solution Heats of NH_4Cl and Specific Heat Capacities of the Solutions at 50°

m $\left(\frac{\text{mole } NH_4Cl}{1000 \text{ g } H_2O}\right)$	0.0122	0.0668	0.1990	0.2049	0.3079	0.5105	0.7948	0.9751	1.2099	1.7938	2.0126	2.2208	2.8254
C_p (cal./g. deg.)	—	—	—	0.985_9	0.980_0	—	—	0.945_8	—	—	0.898_0	—	—
ΔH_m (cal./mole)	2774	2868	2888	—	—	2954	3009 *	—	3025 *	3070 *	—	3109 *	3115 *

m $\left(\frac{\text{mole } NH_4Cl}{1000 \text{ g } H_2O}\right)$	3.2712	3.5869	3.8646	4.3727	4.8948	5.0476	5.5837	6.0353	7.0116	7.0173	7.4780	7.9448	8.5231	9.0051	9.1187
C_p (cal./g. deg.)	—	0.842_8	—	—	—	0.800_9	—	—	0.757_5	—	—	—	—	—	0.718_2
ΔH_m (cal./mole)	3132 *	—	3157 *	3183 *	3175 *	—	3212 *	3205 *	—	3240 *	3248 *	3246 **	3273 *	3236 *	—

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* ΔH_m was obtained from the intermediate solution heats.

** ΔH_m was obtained from the dilution heats.

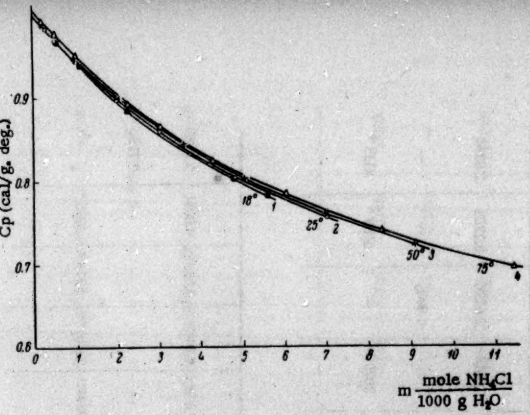

Fig. 1. Specific heat capacities of NH_4Cl solutions in water.*

initial solution heats, ΔH_0, at 25°, we used the above-indicated data of Streeck [28] on dilution heats. Such data fail to exist for 50 and 75°, for which reason we determined the initial solution heats at these temperatures by the less accurate extrapolation of our data from m = 0.12 at 50° and from m = 0.051 at 75° to m = 0.

Purification of the Salt. We used commercial ammonium chloride labeled "pure reagent" and "pure". The salt was recrystallized three times (the last time from double-distilled water), where NH_4OH [35] was added to the solution to precipitate any iron and to prevent hydrolysis of the salt during boiling. The obtained crystals were dried at 50-60°, ground, and kept in a desiccator in a ground glass stoppered bottle. The absence of excess HCl was shown when the salt was checked for neutrality. In our work we used ordinary laboratory distilled water. In later experiments we became convinced that NH_4Cl that had been recrystallized twice from ordinary distilled water shows the same solution heat.

Discussion of Results

The data obtained by us for the specific heat capacities of the system NH_4Cl - H_2O and the integral solution heats of NH_4Cl in water at 25, 50, 75° are summarized in Tables 1-3 and plotted in Figs. 1 and 2.

TABLE 3

Integral Solution Heats of NH_4Cl and Specific Heat Capacities of the Solutions at 75°

m $\left(\frac{\text{mole } NH_4Cl}{1000 \text{ g } H_2O}\right)$	0.0508	0.1921	0.2023	0.3013	0.3892	0.4920	0.5573	0.7718	1.0033
C_p (cal./g. deg.)	—	0.989_6	—	—	—	0.976_4	—	—	0.950_0
ΔH_m (cal./mole)	2258	—	2312	2314	2324	—	2344	2400	—

m $\left(\frac{\text{mole } NH_4Cl}{1000 \text{ g } H_2O}\right)$	2.2545	3.0315	3.4651	4.3083	6.0441	6.4990	8.3118	10.0395	11.4398
C_p (cal./g. deg.)	0.890_3	0.862_7	—	0.823_8	0.781_8	—	0.736_9	—	0.693_4
ΔH_m (cal./mole)	—	—	2640**	—	—	2948**	—	3074**	—

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* 1) Thomsen's data [25], 2-4) authors' data.

** ΔH_m was obtained from the dilution heats.

The heat capacity isotherms appear as sloping, nearly parallel, curves without any characteristic points. The heat capacity temperature coefficient is very small and is ~ 0.00017 cal./g·deg.^2 (from the data of Urban [36] in the interval 20-40°, for m = 2, $\frac{dCp}{dT}$ = 0.00021 cal./g·deg.^2). In Fig. 1, in addition to our data on the heat capacities of NH_4Cl solutions in water at 25, 50 and 75°, we have plotted the 18° isotherm studied by Thomsen [25], without the doubtful final point.

The solution heat isotherms, $\Delta H_m = f(m)$, are shown in Fig. 2. Comparison of our data with the combined 18° isotherm of Bichowsky and Rossini [4] gave a highly improbable intersection of the 18 and 25° isotherms at $m \approx 4$ (Fig. 2). A familiarization with the sources used by Bichowsky and Rossini revealed that in the region of high concentrations they took the unreliable data of Mondain-Monval (which were critically analyzed by us above). Consequently, it was necessary for us to run a series of experiments on the determination of the integral solution heats of NH_4Cl at 18° from direct measurements and from the intermediate dilution heats. The results of these experiments are summarized in Table 4. A comparison of our direct measurement results of ΔH_m at m = 0.523 with the handbook data showed satisfactory agreement: our data, ΔH_m = 3920 ± 11 cal./mole; handbook data, 3930 cal./mole.

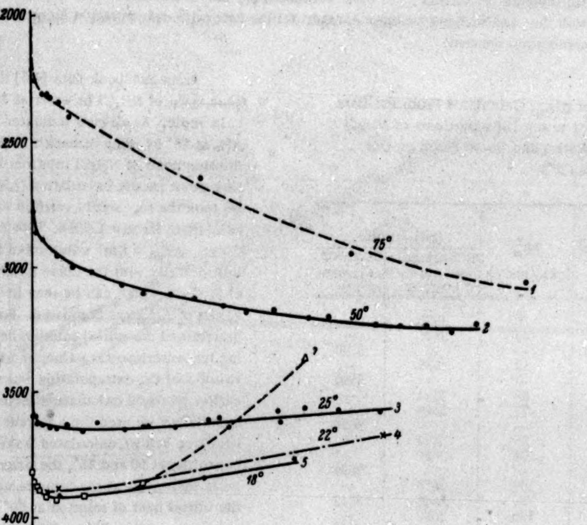

Fig. 2. Integral solution heats of NH_4Cl in water.
1-3) Data of the authors, 4) data of [24], 5) our corrected 18° isotherm (dots – our data, squares–data of [5], triangle–point of Mondain-Monval [22]), 6) data of [20].

The difference lies within the limits of measurements error. Our considerations relative to Mondain-Monval's data are also supported by the few measurements made made by A. S. Fedorov and G. V. Silchenko [24] at 22° (Fig. 2).

For the reasons given above, the 0° isotherm obtained by Lehtonen is shown as a dotted line in the same graph. The disposition and shape of this isotherm is in full accord with the others. Our 75° isotherm is also shown as a dotted line, since it was studied in insufficient detail and with a lower accuracy than the others. However, the general character of its course must be considered as being firmly established.

TABLE 4
Integral Solution Heats of NH_4Cl a

$m\left(\frac{\text{mole}NH_4Cl}{1000\,g\,H_2O}\right)$	0.523	3.465	5.324
ΔH_m (cal./mole)	3920	3851 •	3776•

• ΔH_m was obtained from the dilution heats.

In examining Fig. 2 attention is attracted to the gradual change in the slope of the isotherms $\Delta H_m = f(m)$ in measure with temperature change, i.e. their transistion (by the classification of K. P. Mishchenko and M. Z. Pronina [1]) from the class showing constant exothermal increase with concentration increase to the class showing constant exothermal decrease.

TABLE 5
Comparison of ΔH_m, Calculated From the Data of Streeck [28] on the Dilution Heats of NH_4Cl Solutions in Water, and Those Based on Our Measurements (25°)

$m\,\frac{\text{mole }NH_4Cl}{1000\text{ g }H_2O}$	ΔH_m^0 (cal./mole)	ΔH_m (cal./mole) calculated from the data of Streeck	ΔH_m (cal./mole) from our measurements
0	0	3526	—
0.0256	49	3575	—
0.0299	—	—	3590
0.0400	59	3585	—
0.0519	—	—	3596
0.0576	68	3594	—
0.0784	77	3603	—
0.1019	—	—	3625
0.1024	85	3611	—
0.1936	104	3630	—
0.2016	—	—	3629
0.2304	109	3635	—
0.3600	120	3646	3642
0.4624	126	3652	—
0.5023	—	—	3648
0.5184	129	3655	—
0.6400	133	3659	—
0.6990	—	—	3634
0.7056	134	3660	—
1.0000	136	3662	—
1.0054	—	—	3662

From handbook data [4,5] the initial solution heat, ΔH_0, of NH_4Cl in water at 18° is equal to 3818 cal./mole. As already indicated above, we found ΔH_0 at 25° by using Streeck's data on the integral dilution heats of NH_4Cl solutions in water. As the base point for the calculation ($\Delta H_0 = \Delta H_m - \Delta H_m^0$) we took the repeatedly verified value $\Delta H_m = 3662$ cal./mole for m = 1.0054. Thus $\Delta H_0 = 3526$ cal/mole. Curve $\Delta H_m = f(m)$ constructed from our data, blends satisfactorily with the curve calculated from the data of Streeck, which can be seen in Table 5, where the values of ΔH_m are compared. For 50 and 75° we determined the initial solution heats by extrapolating the experimental values of ΔH_m to m = 0. The validity of the extrapolation was verified by our earlier proposed calculation method [37]. For the calculation we used the apparent molal heat capacities (see below), calculated from the specific heat capacities at 50 and 75°, the latter being more reliable than ΔH_m at the same temperatures. We took the initial heat of solution at 50° as equal to 2726 cal./mole, and at 75° as 2050 cal./mole.••

With the purpose in mind of utilizing thermochemical data to evaluate the structure of electrolyte solutions we subjected experimental material to a special treatment. Even D. I. Mendeleev had mentioned that the rules, hidden in studying integral functions, frequently become evident in differential functions [38]. Acknowledgment of the validity of such a postulation was expressed in a utilization of the so-called partial molal (p.m.) values [39].

We calculated for 18, 25, 50 and 75° the apparent heat capacities (ΦCp), the p.m. heat capacities of NH_4Cl in the system NH_4Cl - H_2O ($\bar{C}p_2$), and the relative p.m. heat capacities of H_2O in the same system ($\bar{C}p_1 - \bar{C}p_1^0$).

•• We needed these data for later treatment of the experimental material.

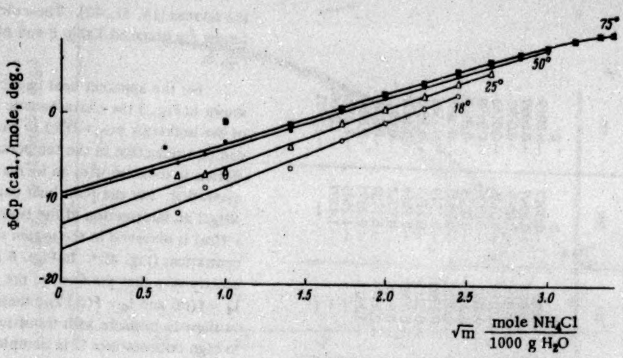

Fig. 3. Apparent molal heat capacities of NH_4Cl in the system NH_4Cl - H_2O.

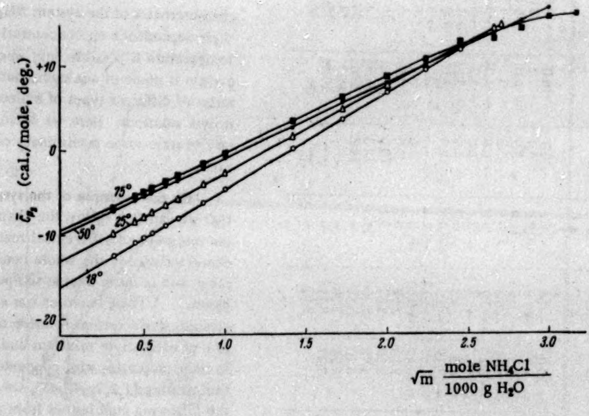

Fig. 4. Partial molal heat capacities of NH_4Cl in the system NH_4Cl - H_2O.

These values are given in Table 6 and plotted in Figs. 3-5. In a similar manner we calculated for the same temperatures the relative p.m. enthalpies of NH_4Cl and H_2O in the system NH_4Cl - H_2O, ($\bar{L}_2$ and $\bar{L}_1$). The calculated data are summarized in Table 7 and shown in Figs. 6 and 7. We used the ordinary graph analysis methods [40] in calculating these values.

Finally, we calculated the so-called nonideal portions of the relative p.m. entropies of H_2O in the system NH_4Cl - H_2O, $(\bar{S}_1 - \bar{S}_1^0)$ nonideal, at the same four temperatures. We obtained these values by substracting from the complete value, $(S_1 - \bar{S}_1^0)$ complete, that portion which is observed when any substances, even ideal, are mixed. This ideal portion of the relative p.m. entropy is calculated from the equation:

$$(\bar{S}_1 - \bar{S}_1^0) \text{ ideal} = - R\ln N_1,$$

where N_1 is the mole fraction of water in the solution. A description of similar calculations can be found in

TABLE 6

Apparent and Partial Molal Heat Capacities of NH_4Cl and H_2O in the System NH_4Cl - H_2O

m $\frac{\text{mole } NH_4Cl}{1000 \text{ g } H_2O}$	$\Phi C_p = \frac{C_p - 55.51\bar{C}^{\circ}_{p_1}}{m}$				$\bar{C}_{p_2} = \Phi C_p + \frac{\sqrt{m}}{2} \cdot \frac{d\Phi C_p}{d\sqrt{m}}$				$\bar{C}_{p_1} - \bar{C}^{\circ}_{p_1} = -\frac{m\sqrt{m}}{2 \cdot 55.51} \cdot \frac{d\Phi C_p}{d\sqrt{m}}$			
	18°	25°	50°	75°	18°	25°	50°	75°	18°	25°	50°	75°
0	−16.1	−13.2	−10.0	−9.6	−16.1	−13.2	−10.0	−9.6	0	0	0	0
0.1	−13.7	−11.0	− 8.1	−7.6	−12.5	− 9.9	− 7.2	−7.0	−0.0023	−0.0021	−0.0017	−0.0019
0.2	−12.7	−10.0	− 7.3	−6.8	−11.0	− 8.5	− 6.0	−5.4	−0.0061	−0.0055	−0.0047	−0.0050
0.3	−11.9	− 9.4	− 6.7	−6.2	− 9.8	− 7.5	− 5.1	−4.5	−0.0114	−0.0104	−0.0089	−0.0093
0.4	−11.3	− 8.8	− 6.2	−5.7	− 9.0	− 6.6	− 4.3	−3.7	−0.0175	−0.0159	−0.0136	−0.0143
0.5	−10.8	− 8.3	− 5.7	−5.3	− 8.1	− 6.0	− 3.7	−3.0	−0.0243	−0.0221	−0.0139	−0.0198
0.75	− 9.6	− 7.1	− 4.8	−4.3	− 6.3	− 4.1	− 2.2	−1.7	−0.0440	−0.0401	−0.0343	−0.0360
1.0	− 8.50	− 6.73	− 3.15	−3.5	− 4.8	− 2.8	− 1.0	−0.4	−0.0683	−0.0622	−0.0533	−0.0558
2.0	− 5.5	− 3.92	− 1.85	−1.17	− 0.1	+ 1.4	+ 2.6	+3.4	−0.1935	−0.1762	−0.1510	−0.1581
3.0	− 3.1	− 0.98	+ 0.47	+0.69	+ 3.5	4.6	5.4	6.2	−0.3529	−0.3213	−0.2753	−0.2883
4.0	− 0.9	+ 0.72	2.13	2.52	6.7	7.6	7.8	8.7	−0.5472	−0.4982	−0.4268	−0.4470
5.0	+ 0.9	2.32	3.50	3.89	9.4	10.0	10.0	10.8	−0.7643	−0.6958	−0.5961	−0.6243
6.0	2.5	3.85	4.98	5.40	11.8	12.3	11.9	12.9	−1.0049	−0.9149	−0.7838	−0.8209
7.0	—	5.20	6.10	6.52	—	14.3	13.6	13.1	—	−1.1526	−0.9875	−0.8340
8.0	—	—	6.94	7.36	—	—	15.3	14.5	—	—	−1.2065	−1.0190
9.0	—	—	7.77	8.11	—	—	16.8	15.8	—	—	−1.4397	−1.2160
10.0	—	—	—	9.07	—	—	—	16.3	—	—	—	−1.2821

the sources [14, 41, 42]. The calculation results are given in Table 8 and plotted in Fig. 8.

For the apparent heat capacities, ΦC_p, shown in Fig. 3 the characteristic approach of the isotherms $\Phi C_p = f(m)$ to each other is due to a reduction in the temperature coefficient in measure with an increase in concentration. For the p.m. heat capacities of NH_4Cl an intersection of the isotherms $C_{p2} = f(m)$ is observed in the region of high concentrations (Fig. 4).* In Figs. 6 and 7 it is clearly seen that the form of the isotherms $\bar{L}_1 = f(m)$ and $\bar{L}_2 = f(m)$ and their change in slope in measure with transition from low to high temperatures is in complete accord with the change in the shapes of the isotherms $\Delta H_m = f(m)$. The same can be said relative to the isotherms $(\bar{S}_1 - \bar{S}_1^0)_{\text{nonideal}} = f(m)$ (Fig. 8).

A detailed evaluation of the energy characteristics of the system NH_4Cl - H_2O and their dependence on concentration and temperature is possible only when a comparison is made of analogous data for a series of different types of aqueous electrolyte solutions. Here we deem it necessary to state some preliminary considerations.

On the example of the system NH_4Cl-H_2O we can first follow the change in both the integral and differential thermodynamic characteristics in the whole concentration range and in quite a wide temperature diapason. Then, based on our earlier expressed considerations relative to the structure of electrolyte solutions and the change in their properties with concentration and temperature [1,2,7a,42,43], we can make the following conclusions from an examination of the data given in this paper.

The above-noted gradual transition of the isotherms of a number of energy properties of the studied system from one class to another when the temperature is raised compels a new glance at the proposed [1] and utilized [7] classification of electrolytic solutions based on the shape of the isotherms $\Delta H_m = f(m)$. Without question

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* This interesting phenomenon, which proves to be general for electrolytic solutions, was described in [45].

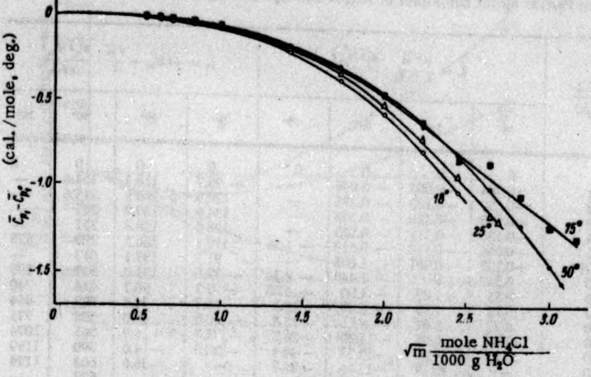

Fig. 5. Relative partial molal heat capacities of H_2O in the system NH_4Cl - H_2O.

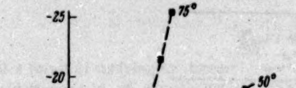

Fig. 6. Relative partial molal enthalpies of NH_4Cl in the system NH_4Cl - H_2O.

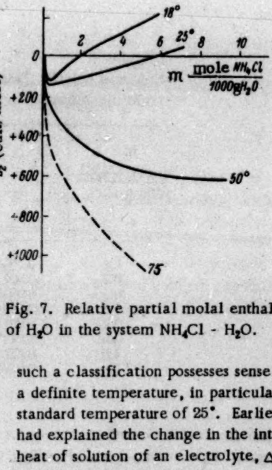

Fig. 7. Relative partial molal enthalpies of H_2O in the system NH_4Cl - H_2O.

such a classification possesses sense only at a definite temperature, in particular at the standard temperature of 25°. Earlier [1] we had explained the change in the integral heat of solution of an electrolyte, ΔH_m, in measure with concentration increase as being due to the dependence of the exo- and endothermic effects of the desolvation of ions (at first energic, and after the limits of complete solvation [43] also coordination) on the concentration, a change in structure of water, and a gradually closer approach of the electrolyte ions to each other. We also explained the temperature coefficients ΔH_m [2] in the light of these

TABLE 7

Relative Partial Molal Enthalpies of NH_4Cl and H_2O in NH_4Cl Solutions

m $\frac{\text{mole } NH_4Cl}{1000 \text{ g } H_2O}$	$\bar{L}_1 = \frac{m\sqrt{m}}{2 \cdot 55.51} \cdot \frac{d(\Delta H^{\circ}_m)}{d\sqrt{m}}$				$\bar{L}_2 = -\Delta H^{\circ}_m - \frac{\sqrt{m}}{2} \cdot \frac{d(\Delta H^{\circ}_m)}{d\sqrt{m}}$			
	18°	25°	50°	75°	18°	25°	50°	75°
0	0	0	0	0	0	0	0	0
0.1	−0.064	−0.064	− 0.096	—	+ 93.7	118.7	164.6	—
0.2	−0.152	−0.120	− 0.224	—	128.5	140.5	215.6	—
0.3	−0.180	−0.120	− 0.378	—	134.9	139.9	247	—
0.4	−0.138	−0.115	− 0.523	—	128.0	138.8	271	—
0.5	−0.064	−0.110	− 0.619	− 1.26	119.1	136.1	282	528
0.75	+0.232	−0.081	− 1.005	—	91.7	137.1	317	—
1.0	0.540	0	− 1.440	− 2.34	+ 72.0	131.0	347	595
2.0	2.55	+1.02	− 4.00	− 6.63	− 2.7	96.7	444	740
3.0	5.12	1.95	− 6.40	−12.1	− 58.7	74.8	498	864
4.0	8.29	3.61	− 8.65	−18.8	−110.0	48.0	532	975
5.0	13.39	6.04	−11.28	−26.2	−174.7	+16.9	565	1074
6.0	18.47	9.27	−13.77	−34.4	−225.9	−14.0	590	1159
7.0	—	12.18	−15.56	−36.7	—	−38.6	603	1174
8.0	—	—	−18.34	—	—	—	622	—
9.0	—	—	−18.92	—	—	—	628	—

TABLE 8

Nonideal Relative Partial Molal Entropies of Water in Ammonium Chloride Solutions

m $\frac{\text{mole } NH_4Cl}{1000 \text{ g } H_2O}$	$(\bar{S}_1 - \bar{S}^{\circ}_1)$ non-ideal $= \frac{\bar{L}_1 - 4.576 \cdot T \cdot \log \frac{a_1}{N_1}}{T}$			
	18°	25°	50°	75°
0.1	−0.00063	−0.00081	−0.00083	—
0.2	−0.00178	−0.00158	−0.00196	—
0.5	−0.00351	−0.00355	−0.00523	−0.0056
1.0	−0.00841	−0.00575	−0.01040	−0.0109
2.0	+0.00118	−0.00430	−0.02032	−0.0280
3.0	0.01152	+0.00020	−0.02638	−0.0433
4.0	0.02676	0.00994	−0.02930	−0.0632
5.0	0.05023	0.02330	−0.02930	−0.0843

representations, and the change in the slopes of $\Delta H_m = f(m)$ with temperature can be explained in the same manner. Apparently, a more general classification of electrolytes can be based, not on the shape of the individual isotherms, but on the temperature zone of the transition from one class to another: the more dominant the solvation effects, the relatively lower should this temperature region lie. From the energy viewpoint the ions NH_4^+ and Cl^- should show comparatively weak solvation;* consequently at low temperatures the exothermic effect of gradually closer approach of the ions to each other will dominate in the studied system, and with increase in concentration the integral heat of solution will become more exothermic (less endothermic). When the temperature is raised the energy of interionic reaction shows comparatively little change, while the endothermic effects of desolvation naturally show a greater change. This leads to the situation that the slope of the isotherms $\Delta H_m = f(m)$ gradually decreases, and at a sufficiently high temperature, changes its sign.

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* $\Delta H_{hNH_4^+} = -79$ kcal./g.-ion; $\Delta H_{hCl^-} = -79$ kcal./g.-ion [44].

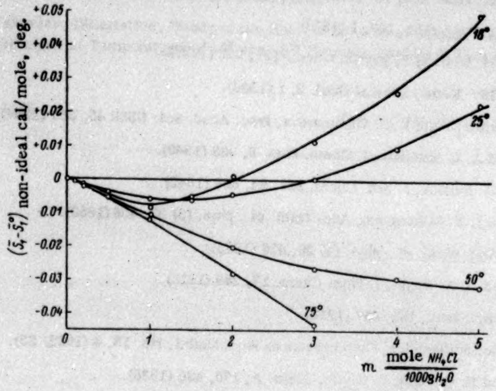

Fig. 8. Nonideal portion of the relative partial molal entropies of H_2O in the system NH_4Cl - H_2O.

The remaining energy characteristics of the concentration and temperature relationships for the systems of interest to us can be satisfactorily explained in the light of the above representations.

SUMMARY

As a result of studying the integral heats of solution of NH_4Cl in water and the heat capacities of the resulting solutions at 18, 25, 50 and 75° we calculated the partial molal thermodynamic characteristics of these solutions and were the first to obtain a picture of the changes of these properties in such a wide interval of concentrations and temperatures. Considerations were expressed relative to the expediency of a thermochemical classification of electrolyte solutions, not by the shape of the individual isotherms, but by the temperature zone of the transition from one type of isotherm to another. The observed phenomena are qualitatively explained in the light of the relative role played by solvation effects, on the one hand, and the effect of closer approach of ions to each other, on the other.

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Received July 5, 1955

Lensovet Leningrad Technological Institute

DECOMPOSITION RATE OF POTASSIUM PERSULFATE IN HYDROCARBON EMULSIONS

A. I. Yurzhenko and O. P. Brazhnikova

Peroxides find extensive use as initiators for the polymerization of unsaturated compounds in emulsions. This initiating action shown by peroxides is associated with their thermal decomposition to free radicals, which incite chain polymerization.

In this connection a study of the decomposition of peroxide initiators under conditions that are either close or identical with those of emulsion polymerization (presence of an emulsifier, surface separation of the emulsion phases, a definite buffer system, regulating the pH of the aqueous phase, etc.) shows essential significance in studying emulsion polymerization processes. At the same time the number of such studies is extremely few. Some results in this direction were obtained by T. Yurzhenko and coworkers [1].

To us it seems impossible to use the data obtained for true solutions (either aqueous or nonaqueous, depending on the nature of the peroxide) in homogeneous medium to evaluate the decomposition of peroxides in emulsion polymerization, since the decomposition kinetics can change under the influence of the factors operating in emulsion polymerization. Evidently this circumstance can explain to a certain degree the lack of agreement observed in a number of cases between the initiating capacity of a peroxide (observed in the emulsion polymerization of a monomer) and its thermal decomposition (observed usually in a homogeneous medium).

In the previous paper [2] we had studied the decomposition kinetics of potassium persulfate in a homogeneous medium at different pH, and also in the presence of electrolytes, including soap and soaplike substances, commonly used in emulsion polymerization. It was shown in particular that colloidal electrolytes (Nekal, sodium oleate) accelerate the decomposition of the studied peroxide, while the usual electrolytes (salts) retard the decomposition.

The purpose of the present work was to study the decomposition rate of potassium persulfate in heterogeneous media – in some hydrocarbon emulsions, in which number polymerizable styrene is included.

EXPERIMENTAL

Method of Operation. We studied the decomposition of potassium persulfate in heterogeneous media in special vessels – ampuls fitted with double seals (Fig. 1), in a water ultrathermostat in a special cradle. The oscillation frequency chosen was such that the formation of hydrocarbon emulsions was assured. The hydrocarbons used were toluene, hexane, α-methylstyrene and styrene. The amount of hydrocarbon taken was 1/10 of the aqueous phase volume.

In some of the experiments the water phase contained Nekal (sodium salt of dibutyl-α-naphthalenesulfonic acid) as emulsifier. To create a definite pH in the aqueous phase we used either sulfuric acid, sodium hydroxide or soda. The amount of peroxide in the original water solution was usually 2 g per 100 g of solvent.

The experiments were run at 70 and 80°. The temperature was maintained constant with an accuracy of 0.02°.

The amount of undecomposed peroxide was determined by iodometric titration of the aqueous phase at definite time intervals. The aqueous phase of the emulsion was separated from the hydrocarbon portion by brief centrifuging of the ampuls after they had been cooled in a mixture of water and ice. The presence of peroxide in the hydrocarbon phase could not be shown.

We took 7-10 ampuls for each experiment, and removed 1-2 ampuls for each titration. The experiments were run in duplicate.

DISCUSSION OF RESULTS

The data on the decomposition rates of potassium persulfate in water solutions and in hexane emulsions are plotted in Fig.2. It can be seen from these data that both in water solutions (without a hydrocarbon) and in heterogeneous medium (hexane emulsion) the decomposition of $K_2S_2O_8$ is a first order reaction, which follows from the linear character of the relationship - log $\underline{c}$ / $\underline{t}$. We observed a similar situation when we used other emulsified hydrocarbons. From the slope tangents of the straight lines - log $\underline{c}$ / $\underline{t}$ we calculated the decomposition rates of the peroxide, which are shown in Table 1.

It can be seen from Table 1 that in the absence of an emulsified hydrocarbon the decomposition of the studied peroxide shows increase with increase in the hydrogen ion concentration. . A similar situation for other media was observed earlier by Kolthoff and Miller [3].

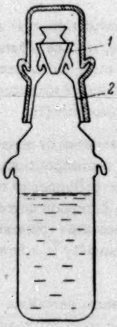

Fig. 1. Vessel for peroxide decomposition in hydrocarbon emulsions.
1) Internal seal, 2) external seal.

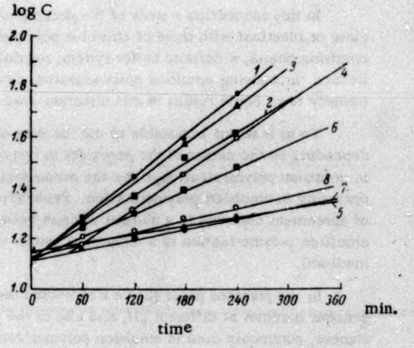

Fig. 2. Relationship between the logarithm of the concentration of $K_2S_2O_8$, in hexane emulsions (straight lines 1-4) and in homogeneous medium (straight lines 5-8), and time at 70°.
1 and 5) pH = 12.4; 2 and 6) pH = 7.3; 3 and 7) pH = 1.3; 4 and 8) pH = 9.8.

It is natural to assume that the first act in the thermal decomposition of $K_2S_2O_8$ in solution is a rupture of the peroxide bond O-O, as being the least stable: $S_2O_8^{2-} \rightarrow 2SO_4^-$.

In the presence of polymerizable hydrocarbons the ions of the SO_4^- radicals are capable of initiating polymerization. In their absence the SO_4^- radicals should suffer the transformation

$$SO_4^- + H_2O \rightarrow HSO_4^- + HO ,$$

$$2HO \rightarrow H_2O + \frac{1}{2} O_2 .$$

As a result, the total process for the decomposition of potassium persulfate in water (either neutral or alkaline medium) can be depicted as follows:

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + \frac{1}{2} O_2 .$$

In acid medium this process is supplemented by the decomposition catalyzed by hydrogen ions and proceeding more rapidly:

$$S_2O_8^{2-} + H_3O^+ \rightarrow [HS_2O_8^- + H_2O] \rightarrow H_2SO_4 + HSO_4^- + \frac{1}{2}O_2.$$

As we had shown earlier [2], the energy of activation for the decomposition of $K_2S_2O_8$ is lower in acid medium than in either alkaline or neutral medium.

As can be seen from Table 1, the decomposition of potassium persulfate in emulsified hydrocarbon emulsions (in the absence of an emulsifier) shows essential increase at all pH values. The acceleration is especially noticeable in alkaline medium, although catalytic decomposition under the influence of hydrogen ions is also retained in the emulsions.

TABLE 1

Decomposition Rate Constants of Potassium Persulfate in Homogeneous and Heterogeneous Media (Hydrocarbon Emulsions Devoid of Emulsifier; Temperature 70°)

Aqueous phase (medium)	pH of the aqueous phase in the starting system	$K \cdot 10^3$ min.$^{-1}$ (aqueous) no hydrocarbon	$K \cdot 10^3$ min.$^{-1}$ (emulsions)		
			hexane	toluene	styrene
0.1 N H_2SO_4 . .	1.3	3.4	5.6	5.2	5.6
Water	7.3	1.8	4.5	3.4	—
0.1 N Na_2CO_3 . .	9.8	1.5	5.0	2.8	3.0
0.1 N NaOH . . .	12.4	1.4	6.3	5.8	—

The fact that the order of the decomposition reaction of potassium persulfate in hydrocarbon emulsions remains the same as in a homogeneous medium does not exclude the direct reaction of $K_2S_2O_8$ with the hydrocarbon molecules. Actually, this reaction should proceed mostly in the aqueous phase (due to the insolubility of $K_2S_2O_8$ in the hydrocarbon phase), while the aqueous phase always remains saturated with hydrocarbon, i.e. its concentration under such reaction would not change, which should fail to lead to a higher reaction order.

It should be mentioned that under our experimental conditions the acceleration of the decomposition reaction in the presence of styrene failed to differ from the same effect observed with the other hydrocarbons, although in the given case the decomposition of the peroxide is accompanied by progress of polymerization and the formation of a polystyrene latex. To be sure, although this process proceeded only slightly due to the absence of an emulsifier, still the SO_4^- radicals that were formed here were definitely consumed in initiating the polymerization process. This circumstance can serve as an indication that the decomposition of $K_2S_2O_8$ is not initiated by the free radicals that appear as decomposition products of the starting peroxide.

TABLE 2

Decomposition Rate Constants of Potassium Persulfate in Nekal-Stabilized α-Methylstyrene Emulsions

pH of the aqueous phase	80°			70°	E (kcal.) in heterogenous medium	E (kcal.) in homogeneous medium [2]
	$K \cdot 10^3$ in aqueous solution	$K \cdot 10^3$ in 2% Nekal solution	$K \cdot 10^3$ in methylstyrene emulsion	$K \cdot 10^3$ in methylstyrene emulsion		
7.1	5.4	8.3	12.7	4.4	25.3	32.5
1.7	10.3	11.2	14.6	5.5	23.3	27.7
9.5	5.2	5.2	6.5	2.0	27.4	30.8

The data on the decomposition of potassium persulfate in Nekal-stabilized methylstyrene emulsions are given in Table 2. Polymerization of the hydrocarbon was absent in the given case. As can be seen from the data in Table 2, although the Nekal emulsifier by itself can accelerate the peroxide decomposition, in the presence of an emulsified hydrocarbon this decomposition is accelerated even more.

It is important to mention that the energy of activation E, calculated by the Arrhenius equation, for the decomposition of potassium persulfate in heterogeneous medium is 4-7 kcal. less than in a homogeneous medium. This shows that rupture of the O-O bond is facilitated in hydrocarbon emulsions.

We can still only postulate that in the given case a definite role is played by the hydrocarbon-water separation surface. Catalytic acceleration of the peroxide decomposition reaction occurs at this surface. Such a postulation stands in accord with a number of facts observed in the emulsion polymerization of unsaturated hydrocarbons.

SUMMARY

1. The decomposition rate of potassium persulfate in various hydrocarbon emulsions was studied. It was found that the equation for a first order reaction satisfactorily describes the decomposition in both homogeneous and heterogeneous media.

2. It was shown that in the presence of emulsified hydrocarbons (including styrene monomer) the decomposition of the peroxide is substantially accelerated at various pH values for the aqueous phase of the emulsions, in which connection this acceleration is accompanied by a 4-7 kcal. reduction in the energy of activation for the decomposition reaction.

It was postulated that the separation surfaces of the phases in an emulsion function as zones for the progress of a catalytic reaction.

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Received June 26, 1955

Lvov Medical Institute

PHYSICOCHEMICAL ANALYSIS OF BINARY SYSTEMS FORMED BY ACETAMIDE WITH ORGANIC ACIDS

I. DENSITY, VISCOSITY, AND ELECTRICAL CONDUCTIVITY OF THE SYSTEM ACETAMIDE-ACETIC ACID

I. M. Bokhcvkin and Yu. I. Bokhovkina

The literature contains very little material about the physicochemical analysis of the binary systems formed by acetamide with organic acids; these investigations, moreover, are of undoubted practical and theoretical interest. Acetamide, like water, is a good solvent for many inorganic and organic substances. Furthermore, due to its high dielectric permeability (59.1), acetamide is capable of ionizing salts, acids and bases dissolved in it.

Solution of organic acids in acetamide results in a process of intensification of electrolytic dissociation with release of an atom of hydrogen; the latter, being a good complex former, facilitates the formation of compounds between the acid and acetamide [1].

TABLE 1

Density of the System Acetamide-Acetic Acid

Content (mole %)		Density		
CH_3COOH	CH_3CONH_2	20°	60°	80°
90	10	1.112	1.036	0.999
85	15	1.118	1.040	1.002
80	20	1.120	1.043	1.006
75	25	1.123	1.046	1.006
70	30	1.125	1.048	1.010
65	35	1.125	1.050	1.012
60	40	0.123	0.048	1.014
55	45	1.120	1.045	1.013
50	50	1.119	1.045	1.016
45	55	—	1.043	—
40	60	—	1.040	1.014
35	65	—	1.040	1.014

TABLE 2

Viscosity of the System Acetamide-Acetic Acid

Content (mole %)		Viscosity (in centipoises)		
CH_3COOH	CH_3CONH_2	20°	60°	80°
90	10	1.954	0.842	0.546
85	15	2.529	0.981	0.592
80	20	3.230	1.116	0.644
75	25	3.990	1.265	0.712
70	30	4.817	1.423	0.772
65	35	5.852	1.567	0.824
60	40	6.659	1.725	0.899
55	45	7.769	1.887	0.974
50	50	8.988	2.059	1.050
40	60	—	2.427	1.170
30	70	—	2.898	1.349

The present paper describes the results that we obtained in the physicochemical investigation of the density, viscosity and electrical conductivity of the system acetamide-acetic acid.

EXPERIMENTAL

The substances were purifed by the usual methods, after which their constants were in good agreement with those reported in the literature. Solutions were prepared by weight and their composition is expressed in molar percentages. Measurements were effected at 20, 60 and 80°. The temperature in the thermostat was kept constant to within ±0.2°.

The viscosity was determined with the help of an Ostwald viscometer and expressed in centipoises. Electrical conductivity was measured by the Kohlrausch method in a closed cell with a smooth platinum electrode. The current source was a lamp generator of sonic frequency with amplifier.

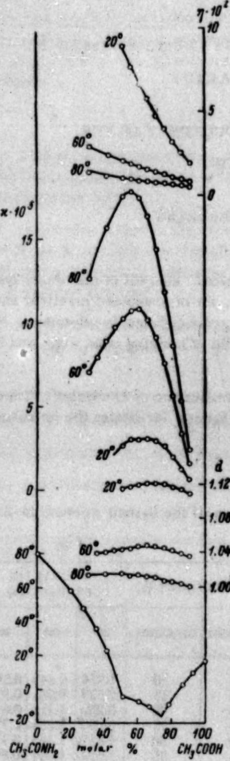

Fig. 1. Summary diagram of properties of the system acetamide-acetic acid

The system acetamide-acetic acid was studied by the fusion method by V. L. Albansky [2] who established the presence of a 1 : 1 compound. His fusion curve is represented in the lower part of Fig. 1. The acetic acid branch descends steeply to the eutectic point which is located at 28.5% acetamide and −17°. The branch of the compound intersecting the acetamide branch at 48.5% acetamide and −2.4° first rises steeply from the eutectic and then gradually.

TABLE 3

Electrical Conductivity of the System Acetamide-Acetic Acid

Content (mole %)		Electrical Conductivity $\kappa \cdot 10^5$			Reduced electrical conductivity $\kappa\eta \cdot 10^5$
CH_3COOH	CH_3CONH_2	20°	60°	80°	60°
90	10	0.638	1.58	2.38	1.33
85	15	1.26	3.38	5.31	3.31
80	20	1.99	5.59	8.60	6.23
75	25	2.60	7.60	11.85	9.61
70	30	2.93	9.15	14.44	13.02
65	35	3.07	10.2	16.4	15.98
60	40	3.07	10.9	17.5	18.80
55	45	3.02	10.7	17.9	20.19
50	50	2.65	10.3	17.6	21.21
45	55	—	9.74	—	—
40	60	—	8.95	15.7	22.51
35	65	—	7.96	—	—
30	70	—	7.11	12.7	21.31

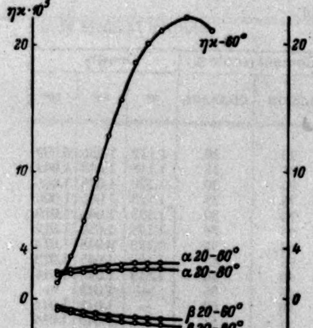

Fig. 2. Isotherms of conductivity at 60°, corrected for viscosity, and curves of the temperature coefficients of electrical conductivity (α) and of viscosity (β) of the system acetamide-acetic acid.

Results of measurements of the density are presented in Table 1 and Fig. 1. The density curves are slightly concave to the axis of composition. Results of measurements of viscosity and specific electrical conductivity are presented in Tables 2 and 3 and plotted in Fig. 1. The viscosity isotherms are convex to the axis of composition. The electrical conductivity isotherms are characterized by a maximum which with rising temperature is slightly shifted towards the acetamide side. A more or less conspicuous inflection corresponding to 40% acetamide occurs on the isotherm of electrical conductivity at 20°.

The temperature coefficients of electrical conductivity are calculated from the formula:

$$\alpha = \frac{1}{\frac{x_1 - x_2}{2}} \cdot \frac{x_2 - x_1}{t_2 - t_1} \cdot 100.$$

The temperature coefficients of viscosity (Table 4) were similarly calculated; due to their negative values, these were plotted below the line of zero values of this property. The curves of the temperature coefficients of electrical conductivity (α) are plotted in Fig. 2. They are slightly concave to the axis of composition. On the same diagram are plotted the curves of the coefficients of viscosity (β) which are convex to the axis of composition.

TABLE 4

Temperature Coefficients of Electrical Conductivity (α) and Viscosity (β)

Content of CH_3CONH_2 (mole %)	α		β	
	20—60°	20—80°	20—60°	20—80°
10	2.12	1.92	1.98	1.87
15	2.28	2.05	2.20	2.06
20	2.37	2.08	2.43	2.22
25	2.45	2.13	2.59	2.32
30	2.57	2.20	2.74	2.41
35	2.68	2.28	2.88	2.51
40	2.80	2.33	2.94	2.54
45	2.79	2.37	3.04	2.59
50	2.95	2.46	3.13	2.63

Evaluation of results. The concavity to the axis of composition on the isotherms of density points to slight contraction in the system acetamide-acetic acid. Some authors [3] associate such a phenomenon with chemical interaction in a system. Others [4] are of the opinion that contraction can also occur in a system in the absence of chemical interaction. Consequently, the isotherms of density should be regarded solely as a background for more characteristic properties. However, the great deviations of the density isotherms from additivity may be said in some measure to favor the hypothesis of chemical interaction in the system.

The viscosity isotherms which are convex to the axis of composition, indicate dissociation of the associated compound in the system. With rising temperature the convexity decreases and the curve at 80° is nearly a straight line.

The curves of specific electrical conductivity are characterized by a maximum. A similar course is observed for the system inorganic salt-water [5] where the rapid drop of electrical conductivity after the maximum with increase of concentration is associated with a sharp rise in viscosity. Our correction for the electrical conductivity of the system acetamide-acetic acid by multiplying by the viscosity did not substantially alter the course of the conductivity isotherms (Fig. 2). Consequently, it does not suffice to associate the change of electrical conductivity solely with the change of viscosity in the present instance.

Apart from this, there is a slight inflection on the curve of electrical conductivity at 20°. We associate this inflection with the existence of the compound detected on the fusion diagram. Consequently, the 1 : 1 compound in the system acetamide-acetic acid is manifested to a very slight extent on the isotherms of density and electrical conductivity and does not appear at all at higher temperatures.

SUMMARY

1. The density, viscosity and electrical conductivity were investigated in the system acetamide-acetic acid at 20, 60 and 80°.

2. The density and viscosity isotherms indicate dissociation of the associated compound, apart from which, against the background of other properties, the density isotherms provide some support for the hypothesis of chemical interaction in the system.

3. The conductivity isotherms have a maximum whose composition is slightly shifted towards higher concentrations of acetamide with rising temperature. In addition a slight inflection is detected on the conductivity isotherm at 20° and corresponds to the 1 : 1 compound on the fusion diagram.

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Received June 7, 1955

Archangel Institute of Forest Technology

PHYSICOCHEMICAL ANALYSIS OF BINARY SYSTEMS FORMED BY ACETAMIDE WITH ORGANIC ACIDS

II. DENSITY, VISCOSITY AND ELECTRICAL CONDUCTIVITY OF THE SYSTEM ACETAMIDE-MONOCHLOROACETIC ACID

Yu. I. Bokhovkina and I. M. Bokhovkin

Results were previously [1] published of a study of the density, viscosity and electrical conductivity of the system acetamide-acetic acid in the fused state, and it was established that the curves of these properties indicate considerable dissociation of the associated compound. In addition, the concave character of the density curves and the presence of a slight inflection on the electrical conductivity curve at 20° are evidence of chemical interaction.

The objective of the present investigation was the elucidation of the character of the interaction of acetamide with monochloroacetic acid. The choice of components was influenced by the desire to establish the effect of an electronegative substituent in the acid radical upon the character of the reaction with acetamide.

TABLE 1

Density in the System Acetamide-Monochloroacetic Acid

Content (mole %)		Density		
CH_3CONH_2	$CH_2ClCOOH$	50°	70°	90°
70	30	—	1.026	1.022
65	35	1.035	1.030	1.027
60	40	1.048	1.034	1.034
55	45	1.042	1.038	1.034
52	48	1.45	1.040	1.036
50	50	1.047	1.042	1.038
48	52	1.049	1.044	1.040
45	55	1.051	1.046	1.042
42	58	1.053	1.048	1.044
40	60	1.055	1.050	1.045
35	65	1.059	1.053	1.049
30	70	1.061	1.057	1.052
25	75	1.064	1.059	1.056

TABLE 2

Viscosity in the System Acetamide-Monochloroacetic Acid

Content (mole %)		Viscosity in centipoises	
CH_3CONH_2	$CH_2ClCOOH$	70°	90°
70	30	1.92	1.13
65	35	1.95	1.15
60	40	1.97	1.16
55	45	1.99	1.17
52	48	1.99	1.18
50	50	2.00	1.18
48	52	2.01	1.18
45	55	2.01	—
42	58	2.02	1.19
40	60	2.00	1.19
35	65	1.98	1.18
30	70	1.95	1.17
25	75	—	1.17

The system acetamide-monochloroacetic acid has been studied by the thermal method [2]. Two compounds were detected in the system: a 1:1 compound with a conspicuous maximum at 8°, and a 1:2 compound with a latent maximum. Two eutectic points were found: the first at 55.1% acetamide and 5.6°, and the second at 45% acetamide and 4.7°; there was also a peritectic point at 34.05% acetamide and 13.2°. The fusion diagram, taken from [3], is shown in the lower part of Fig. 1.

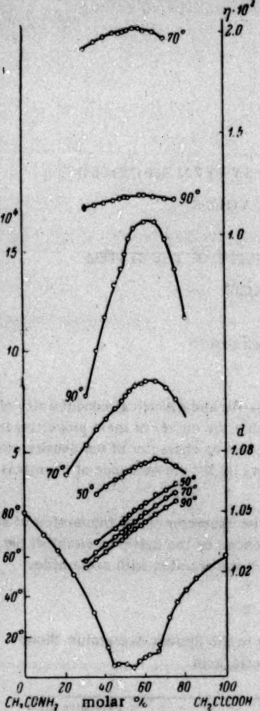


Fig. 1. Fusibility, density (d), electrical conductivity (κ) and viscosity (η) in the system acetamide-monochloroacetic acid.

TABLE 3

Temperature Coefficients of Electrical Conductivity (α) and Viscosity (β)

Content of $CH_2ClCOOH$ (in mole %)	α		β	
	50—70°	50—90°	50—70°	50—90°
35	3.69	2.80	3.80	2.90
40	3.44	2.84	3.73	2.89
45	3.37	2.89	3.72	2.88
48	3.41	2.93	3.77	2.88
50	3.33	2.92	3.77	2.88
52	3.36	2.98	3.76	2.89
55	3.30	2.95	3.74	—
58	3.19	—	3.73	2.87
60	3.17	2.89	3.87	2.92
65	3.00	2.83	3.79	2.87
70	2.95	2.77	3.73	2.84
75	2.85	2.71	—	—

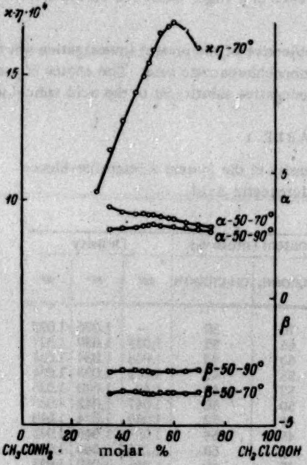


Fig. 2. Reduced electrical conductivity ($\kappa\eta$), temperature coefficient of electrical conductivity (α) and temperature coefficient of viscosity (β) in the system acetamide-monochloroacetic acid.

As in the preceding paper [1], the specific electrical conductivity was measured in a closed cell with a smooth platinum electrode, the viscosity in an Ostwald viscometer, and the density with a pycnometer. The acetamide was purified by recrystallization from ether, and the monochloroacetic acid by distillation; the latter was kept in a desiccator over sulfuric acid. Solutions were prepared by weight, and their composition expressed in mole %. Measurements were performed at 50, 70 and 90°.

Results of determinations of density are presented in Table 1 and Fig. 1. The density isotherms at 50° are curves which are slightly concave to the axis of composition. At 70 and 90° the density isotherms nearly coincide with the additive straight lines. Results of measurements of viscosity are set forth in Table 2 and plotted in the summary composition/property diagram (Fig. 1). The viscosity isotherms are curves which slope down to the axis of composition. The maximum is at 45% acetamide. According to the generally accepted interpretation of viscosity isotherms [3], curves of this type indicate chemical reaction in the system. The curve of temperature coefficient of viscosity versus composition (Table 3, Fig. 2) has a minimum at 50% acetamide.

TABLE 4

Electrical Conductivity in the System Acetamide-Monochloroacetic Acid and Reduced Electrical Conductivity at 70°

Content (in mole %)		Specific electrical conductivity (in $ohm^{-1} \cdot 10^4$)			Reduced electrical conductivity
CH_3CONH_2	$CH_2ClCOOH$	50°	70°	90°	$\kappa \cdot \eta \cdot 10^4$
70	30	—	5.33	7.74	10.24
65	35	2.81	6.10	10.0	11.92
60	40	3.21	6.59	11.7	13.04
55	45	3.54	7.14	13.3	14.24
52	48	3.68	7.49	14.1	14.91
50	50	3.87	7.74	14.8	15.49
48	52	3.94	7.94	15.6	15.99
45	55	4.15	8.24	16.1	16.62
42	58	4.30	8.33	—	16.85
40	60	4.38	8.45	16.4	16.97
35	65	4.53	8.42	16.4	16.68
30	70	4.43	8.15	15.5	15.9
25	75	4.15	7.47	14.0	—
25	80	—	—	11.6	—

Data for measurements of the specific electrical conductivity are presented in Table 4 and Fig. 1. The temperature coefficient of electrical conductivity was calculated with the help of the previously used formula [1]. Data are set forth in Table 3 and plotted in Fig. 2.

Evaluation of Results

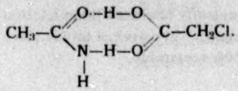
The density isotherms, concave to the axis of composition, indicate slight contraction in the system, evidently associated with chemical interaction of the components [4]. The viscosity isotherms, concave to the axis of composition and passing through a maximum, indicate the existence in the fused homogeneous medium of a compound $CH_3CONH_2 \cdot CH_2ClCOOH$. With rising temperature up to 90°, the maximum becomes diffuse, which indicates relative instability of the compound. The temperature coefficient of viscosity has a minimum corresponding to the compound $CH_3CONH_2 \cdot CH_2ClCOOH$.

The isotherms of electrical conductivity at all the investigated temperatures have a maximum which is slightly shifted in the direction of acetamide with rising temperature. Correction of the electrical conductivity for viscosity does not substantially alter the course of the curve of the reduced electrical conductivity (Fig. 2). At the same time two discontinuities are observed on the curve of specific electrical conductivity at 50 and 70°. The first discontinuity corresponds to the 1:1 compound detected on the fusion diagram; the second corresponds to the compound $2CH_2ClCOOH \cdot CH_3CONH_2$. A discontinuity is observed on the electrical conductivity isotherm at 90° which corresponds to the 1:1 compound. The temperature coefficient of electrical conductivity has a maximum corresponding to the 1:1 compound.

Consequently, the introduction of chlorine into the acetic acid radical increases the stability of the 1:1 compound and leads to appearance of the unstable compound $2CH_2ClCOOH \cdot CH_3CONH_2$.

The structure of compounds of the 1:1 type is explicable from the standpoint of the theory of the hydrogen bond. Acetamide functions as a donor of one pair of electrons and resembles urea in this respect; the latter behaves in a similar manner with derivatives of acetic acid [5].

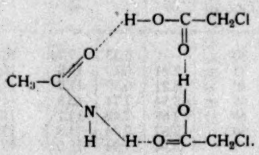
The formation of compounds of the 1:1 type may be schematically represented as follows:



On the assumption of the presence of a hydrogen bond, we can also conceive of the formation of the 2:1 compound.

In this mechanism we must evidently take into consideration the processes of association occurring with carboxylic acids [6].

The formation of 2:1 compounds between acetamide and monochloroacetic acid may be represented:



Acetamide here functions as a donor of one pair of electrons, but it is accepted by the dimer of the second component. Compounds of this type are obviously unstable and break down when the temperature rises. It is understandable that they are weakly reflected on the isotherms of properties in the homogeneous fused medium and that the characteristic discontinuities disappear with rising temperature.

SUMMARY

1. The density, viscosity and specific electrical conductivity in the system acetamide-monochloroacetic acid were investigated at 50, 70 and 90°.

2. The isotherms of electrical conductivity, viscosity and density, as well as the curves of the temperature coefficients of the first two properties, reveal signs of the existence of the compound $CH_3CONH_2 \cdot CH_2ClCOOH$.

3. The isotherms of electrical conductivity at 50 and 70° exhibit discontinuities corresponding to a 2:1 compound, while the isotherms of viscosity and density and the temperature coefficients of the first two properties give no indication of the formation of such a compound.

4. A scheme is put forward for the formation of compounds between acetamide and monochloroacetic acid, based on the concept of the hydrogen bond.

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Received June 7, 1955

Archangel Institute of Forest Technology

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*T.p. = C. B. Translation pagination.

INVESTIGATION OF THE REACTION OF ACETAMIDE WITH SOME AROMATIC ACIDS BY THE METHODS OF PHYSICOCHEMICAL ANALYSIS

Z. K. Dzhelomanova, N. Z. Rudenko and D. E. Dionisyev

In this paper we present the results of a study by the methods of physicochemical analysis of four binary systems formed by acetamide with benzoic, cinnamic, salicylic and anthranilic acids.

The choice of the second components was influenced by the desire to trace the influence on the character of the interaction with acetamide of substitution of hydrogen atoms of the ring in the ortho-position by hydroxy and amino groups. It was also desired to establish to what extent the chemical interaction is affected by the distance of the aromatic nucleus from the carboxyl group.

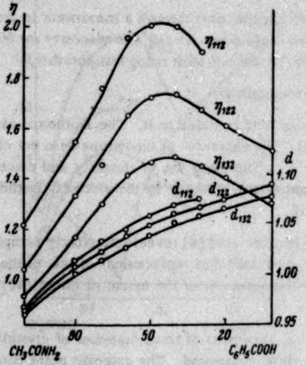

Fig. 1. Viscosity and density of the system acetamide-benzoic acid.

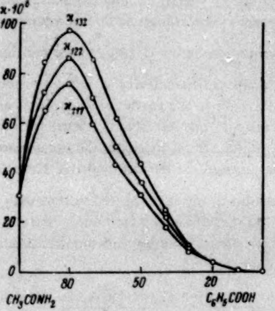

Fig. 2. Electrical conductivity of the system acetamide-benzoic acid.

The systems were studied by measurements of fusibility, density, viscosity and electrical conductivity. The procedure has been described [1]. Curves of properties in the liquid phase were plotted at several temperatures. Concentrations are expressed throughout in molar percentages; viscosities are in centipoises.

The acetamide used in the experiments had m.p. 79.5°; its purification is described in the preceding communication [2]. Benzoic acid was purified by the method given in [3] and had m.p. 121.1°. Trans-cinnamic acid, chemically pure grade, had m.p. 133° after purification.

Salicylic acid melted at 156° and was purified as described in [4]. Anthranilic acid had m.p. 145° after recrystallization from water.

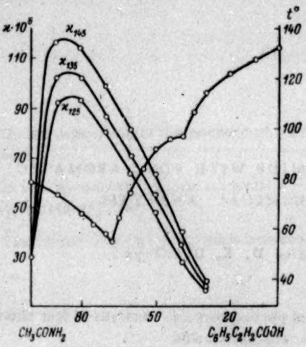

Fig. 3. Electrical conductivity and fusibility of the system acetamide-cinnamic acid.

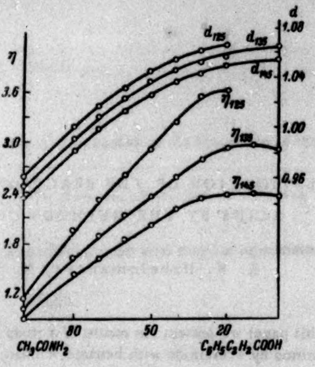

Fig. 4. Viscosity and density in the system acetamide-cinnamic acid.

System Acetamide-Benzoic Acid. Timmermanns [5] studied the fusibility of this system and obtained a phase diagram with a simple eutectic. We studied the system in the liquid phase at 112, 122 and 132°.

The isotherms of viscosity (η) rise steeply (Fig. 1) from the acetamide, pass through a maximum in the region of 50 mole % acetamide and descend gradually to the benzoic acid side. At 112° the viscosity for 50 mole % is nearly twice as high as that of acetamide; the maximum flattens out with rising temperature.

The density isotherms d (Fig. 1) are concave to the axis of composition.

The electrical conductivity κ of acetamide rises when benzoic acid is added to it. The isotherms pass through a maximum in the region of 80 mole % acetamide (Fig. 2). The character of the curves does not change when the electrical conductivity is corrected for the viscosity (κ · η). The sharp rise of viscosity and electrical conductivity in the system indicates the occurrence of chemical interaction. Judging by the viscosity isotherms the compound formed has the composition $CH_3CONH_2 \cdot C_6H_5COOH$.

Comparison of the investigated system with the system urea-benzoic acid [4] reveals the nearly complete similarity of the corresponding isotherms. It follows from what has been said that replacement of one of the amino groups in urea by methyl (acetamide) does not affect either the character or the extent of chemical reaction with benzoic acid.

System Acetamide-Cinnamic Acid. The fusibility curve (Fig. 3) consists of three branches of crystallization: two for the pure components and one for an incongruently melting compound. The eutectic point corresponds to 67 mole % acetamide and 56°. The transition point corresponds to 40 mole % acetamide and 98°. Unlike the preceding system, the fusibility curve reflects the existence of a compound. Its probable composition is $CH_3CONH_2 \cdot 2C_6H_5C_2H_4COOH$, i.e., the same as for urea with fatty acids [6].

Measurements were performed in the liquid phase at 125, 135 and 145°. The viscosity isotherms (Fig. 4) are concave to the axis of composition; the largest deviation from additivity is observed in the region of high concentration of cinnamic acid. The density isotherms (Fig. 4) are concave to the axis of composition.

The electrical conductivity of acetamide rises considerably even when small amounts of cinnamic acid are added and reaches a maximum at 90 mole % acetamide (Fig. 3). Correction of the electrical conductivity for viscosity (κ · η) does not alter the character of the electrical conductivity isotherms.

The character of the isotherms of viscosity, density and electrical conductivity testify to chemical interaction in the system, although the position of the characteristic points does not permit a conclusion about the composition of the compound.

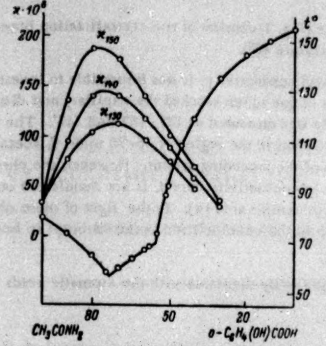

Fig. 5. Electrical conductivity and fusibility of the system acetamide-salicylic acid.

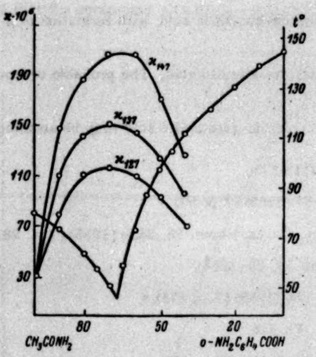

Fig. 7. Electrical conductivity and fusibility of the system acetamide-anthranilic acid.

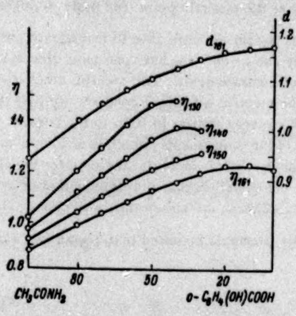

Fig. 6. Viscosity and density of the system acetamide-salicylic acid.

System Acetamide-Salicylic Acid. The fusibility curve consists of three branches (Fig 5): two for the pure components and one for an incongruently melting compound, probably of 1:1 composition. The eutectic point is at 73 mole % acetamide and 56°. The transition point is at 56 mole % acetamide and 70°.

In Fig. 6 are plotted the isotherms of viscosity at 130, 140, 150 and 161°. At low temperatures they pass through a maximum in the region of 40 mole % acetamide. With rising temperature the maximum flattens and disappears completely on the 161° isotherm.

The isotherms of density are concave to the axis of composition. Only one density isotherm is plotted in Fig. 6 (at 161°) since the others, due to the very low temperature coefficient of density, nearly coincide with it.

The electrical conductivity curves (Fig. 5) have a well-defined maximum corresponding to the region of 70-80 mole % acetamide. Correction of the electrical conductivity for the viscosity does not alter the position of the maximum.

On the basis of the above data it may be assumed that the incongruently melting compound of acetamide with salicylic acid can be detected in the liquid phase.

According to our ideas the introduction in the ortho position of a hydroxy group in the benzoic acid molecule must intensify the chemical reaction with acetamide. Investigation of the fusibility in part confirmed this theory, but in the liquid phase the compound of acetamide with salicylic acid is more dissociated than the corresponding compound with benzoic acid, as is shown by the viscosity isotherms.

It is an interesting fact that urea behaves more actively in reaction with salicylic acid [4,7].

System Acetamide-Anthranilic Acid. The fusibility curve (Fig. 7) consists of two crystallization branches, intersecting at the eutectic point (68 mole % acetamide, temperature 48°).

In this system we were able to investigate only the electrical conductivity; it was impossible to investigate the viscosity due to the slow but continuous liberation of bubbles of gas which blocked the capillary and distorted the results of measurements. The specific electrical conductivity was measured at 127, 137 and 147°. The isotherms of the specific electrical conductivity pass through a maximum in the region of 65-75 mole % acetamide (Fig. 7) and are very similar in form to the corresponding curves of the preceding system. However, the chemical interaction of the components, which is reflected on the electrical conductivity curves, is not manifested on the fusibility curves, as is indeed also the case for the system urea-anthranilic acid [4]. In the light of these observations, we can conclude that the introduction of an amino group in the ortho position to the carboxyl in benzoic acid slightly weakens the susceptibility to chemical interaction.

Finally, it should be noted that acetamide reacts less energetically than urea with the aromatic acids studied.

SUMMARY

1. A study was made of the fusibility, viscosity, density and electrical conductivity of the systems of acetamide with benzoic, cinnamic, salicylic and anthranilic acids.

2. The occurrence of chemical interaction in the system acetamide-benzoic acid was established, with formation of the compound $CH_3CONH_2 \cdot C_6H_5COOH$.

3. Chemical interaction was established in the system acetamide-cinnamic acid, with formation of a compound, probably $CH_3CONH_2 \cdot 2C_6H_5C_2H_4COOH$.

4. Chemical interaction was established in the system acetamide-salicylic acid. The probable composition of the compound is $CH_3CONH_2 \cdot HOC_6H_4COOH$.

5. The occurrence of chemical interaction in the system acetamide-anthranilic acid may be assumed.

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Received March 26, 1955

Rostov-on-Don State University

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PHYSICOCHEMICAL ANALYSIS OF THE REACTION OF AMINES WITH ACIDS

III. THERMAL ANALYSIS OF THE TERNARY SYSTEM UREA-FORMIC ACID-WATER

M. N. Kuznetsova and A. G. Bergman

Urea forms salt-like addition compounds with acids. Strong acids [HNO_3, HCl, $C_6H_2OH(NO_2)_3$, etc.] form predominantly 1:1 compounds with urea. According to the literature [1], some of these compounds are decomposed by water. Thermal analysis of the systems of urea with fatty acids showed that in melts the components form compounds, chemical interaction being clearly manifested with formic, acetic and propionic acids [2]. Compounds of urea of the 1:2 type were detected with these acids; their stability fell with increasing molecular weight of the acid. Our earlier examination by thermal analysis of the ternary system urea-acetic acid-water showed that the compound $CO(NH_2)_2 \cdot 2CH_3COOH$ is not decomposed by water and may be recrystallized from water [3].

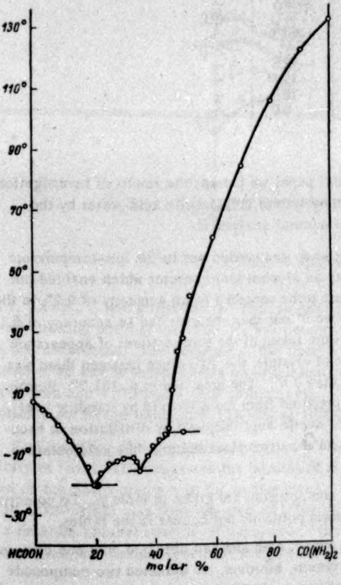

Fig. 1. Fusion diagram of the system HCOOH–$CO(NH_2)_2$.

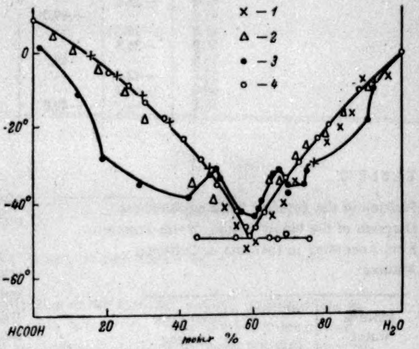

Fig. 2. Fusibility diagram of the system HCOOH–H_2O. 1) Kremann's data [5], 2) Faucon's data [4], 3) Glagoleva's data [6] and our data. (All data are converted to molar percentages).

Little study has been devoted to the problem of the stability of compounds of urea with acids in presence of water. We decided to make a systematic study of this problem with special reference, in the first place, to compounds of urea with aliphatic acids, using both the method of thermal analysis and the methods of investigation of the homogeneous state of systems.

TABLE 1

Melting Points of Mixtures of Urea and Formic Acid

Mole % urea	Melting point	Mole % urea	Melting point	Mole % urea	Melting point	Mole % urea	Melting point
0.0	7.4	22.0	—16.3	38.0	—10.5	50.0	32.5
5.0	3.0	25.0	—13.4	40.0	— 7.4	60.0	60.8
8.0	— 0.2	28.0	—12.2	42.0	— 5.5	70.0	84.1
12.0	— 5.4	30.0	—11.6	44.0	— 3.5	80.0	105.6
15.0	— 8.9	33.3	—11.5	44.5	— 3.0	90.0	122.5
18.0	—14.1	34.0	—12.8	45.0	— 1.6	100	132.5
20.0	—20.2	35.0	—15.5	46.0	10.7	—	—

TABLE 2

Melting Point of Mixtures of Formic Acid and Water

Mole % water	Melting point	Temperature of eutectic halt	Mole % water	Melting point	Temperature of eutectic halt
0.0	8.3	—	59.0	—48.5	—
20.0	— 5.6	—	60.2	—46.8	—
25.2	— 8.2	—	63.0	—43.0	—
30.5	—13.0	—	64.2	—	—49.0
35.5	—17.3	—	66.6	—	—50.0
41.0	—23.2	—	68.3	—33.5	—
45.0	—	—49.0	68.8	—	—49.0
45.8	—28.3	—	72.0	—29.3	—
50.0	—35.3	—	75.0	—	—50.0
55.0	—	—49.5	76.9	—22.8	—
55.4	—42.0	—	80.0	—19.7	—
58.0	—46.7	—	88.0	—10.3	—
58.5	—	—49.0	100.0	0.0	—

TABLE 3

Position of the Eutectic Point on the Phase Diagram of the Binary System Water-Formic Acid According to the Data of Different Authors

Mole % water	Melting point of mixture	Literature source
58.00	—48.00	[4]
58.95	—53.5	[5]
42.00	—39.9	[6]
49.80	—44.6	
31.1	—39.6	
59.0	—48.5	[2, 3]

In this paper we present the results of investigation of the ternary system urea-formic acid-water by the method of thermal analysis.

The work was carried out in the low-temperature region with an alcohol thermometer which enabled the temperature to be recorded to an accuracy of 0.2°; in the region above 0° our thermometer had an accuracy of 0.1°. Readings were taken of the temperatures of appearance and fusion of crystals; the difference between them was not more than 0.5°. The urea had m.p. 132.7°. Formic acid was prepared from the 85% acid by standing over dehydrated oxalic acid followed by distillation in vacuum at 74-76° in a ten-plate column; the acid obtained had m.p. 8.3°.

All compositions are given in mole %. To conserve space, certain points do not appear in the tables.

We had previously studied the fusibility of the system urea-formic acid and had detected only one compound of the 1:2 type [2]. On repeating the investigation of this binary system, however, we detected two compounds: $CO(NH_2)_2 \cdot 2HCCOH$ with a pronounced maximum and $CO(NH_2)_2 \cdot HCOOH$ with a transition point

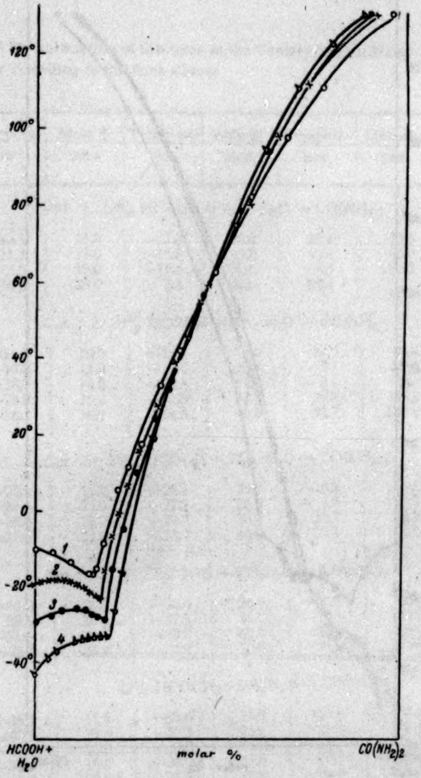

Fig. 3. Fusion diagram of the ternary system (Cuts 1-4).

(Fig. 1, Table 1). We attributed the error in our first investigation to the fact that, starting from 40 mole % urea the melting point of the mixtures was determined at 10 mole % intervals; consequently, the transition point was undetected. The presence of the transition point was proven by study of the cooling curves for compositions of 45 and 50 mole % urea on which halts were observed at −3.0°. Eutectics occur at 20.0 and 35.0 mole % urea and −20.2 and −15.5° respectively. The compound $CO(NH_2)_2 \cdot 2HCOOH$ melts at −11.5°. The transition point of the compound $CO(NH_2)_2 \cdot HCOOH$ is at 44.5% urea and −3°.

The fusibility of the system water-formic acid has previously been investigated [4,5]. The high hygroscopicity of formic acid suggested the possibility of the existence of hydrates, but only one eutectic point appeared on the fusion diagram in the studies cited. The presence in the system of two hydrates $HCOOH \cdot H_2O$ and $HCOOH \cdot 2H_2O$ was later reported [6], but these claims have not yet been confirmed; we therefore undertook a detailed thermal analysis of the system. Our results (Table 2, Fig. 2) confirmed the eutectic character of the diagram and are in agreement with [4,5].

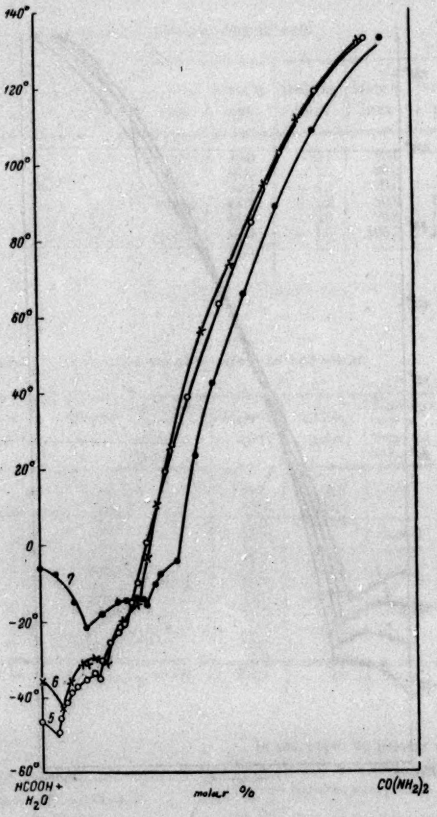

Fig. 4. Fusion diagram of the ternary system (Cuts 5-7).

Comparative data for the position of the eutectic point in this system are set forth in Table 3.

The discrepancies between the results of determinations of the eutectic point by different authors are explained by the occurrence of fairly strong supercooling. Mixtrues at low temperatures were entirely permeated by extremely fine air bubbles, and this too could lead to errors in the observation of crystallization.

The system water-urea has been investigated by a number of authors [7-11] who found a eutectic point with similar constants. Our data indicate a eutectic at 12.7 mole % urea and -11.5°.

In plotting the diagram of the ternary system we investigated 13 sections, 7 of which were at the urea corner (Figs. 3 and 4, Table 4) and 6 at the water corner (Figs. 5 and 6, Table 5). The constructed projection of the diagram, on which the isotherms are plotted at 10° intervals (Fig. 7), comprises 5 fields of crystallization: 3 fields of components and 2 fields of compounds:

$$CO(NH_2)_2 \cdot 2HCOOH \text{ and } CO(NH_2)_2 \cdot HCOOH.$$

TABLE 4

Temperatures of Crystallization of Mixtures in the Ternary System Water-Urea-Formic Acid in Sections Extending to the Urea Corner

Mole % urea	Temperature	Mole % urea	Temperature	Mole % urea	Temperature	Mole % urea	Temperature
Cut 1: 12% HCOOH + 88% $H_2O \rightarrow CO(NH_2)_2$							
0.0	−10.3°	16.0	−17.0°	30.0	22.4°	70.0	99.6°
5.0	−11.3	17.0	−15.5	40.0	43.0	80.0	113.0
10.0	−13.3	19.0	−18.3	50.0	63.5	100.0	132.7
15.0	−16.3	23.0	5.4	60.0	83.4		
Cut 2: 20% HCOOH + 80% $H_2O \rightarrow CO(NH_2)_2$							
0.0	−19.7	10.0	−18.6	19.0	−22.7	50.0	59.8
2.0	−19.0	12.0	−19.6	20.0	−15.5	60.0	80.2
4.0	−18.2	14.0	−20.1	24.0	− 0.5	70.0	99.3
6.0	−18.2	16.0	−21.5	30.0	16.0	80.0	113.2
8.0	−18.2	18.0	−22.3	40.0	39.7	100.0	132.7
Cut 3: 28% HCOOH + 72% $H_2O \rightarrow CO(NH_2)_2$							
0.0	−29.3	15.0	−26.1	23.0	−15.8	50.0	57.3
5.0	−27.4	17.0	−27.2	26.0	− 4.8	60.0	79.5
8.0	−26.0	19.0	−27.9	30.0	10.3	70.0	90.3
12.0	−25.6	21.0	−28.7	40.0	34.5	80.0	112.0
Cut 4: 37% HCOOH + 63% $H_2O \rightarrow CO(NH_2)_2$							
0.0	−43.0	16.0	−33.0	26.0	−16.5	60.0	75.4
4.0	−38.5	20.0	−32.5	35.0	19.5	70.0	95.2
6.0	−36.5	22.0	−32.2	40.0	32.6	80.0	111.5
12.0	−33.7	24.0	−26.7	50.0	55.0	90.0	124.7
Cut 5: 42% HCOOH + 58% $H_2O \rightarrow CO(NH_2)_2$							
0	−46.7	15.0	−35.6	24.0	−23.2	38.0	19.2
5.7	−49.8	17.0	−33.5	25.0	−21.5	55.0	63.3
8.0	−41.7	18.0	−35.2	26.0	−21.0	65.0	84.8
10.0	−38.9	19.0	−30.0	28.0	−15.1	75.0	102.5
12.0	−37.2	22.0	−25.5	30.0	−10.0	85.0	119.0
Cut 6: 50% HCOOH + 50% $H_2O \rightarrow CO(NH_2)_2$							
0.0	−35.3	17.0	−29.5	24.2	−20.5	40.0	26.0
7.0	−42.7	18.0	−29.0	25.9	−19.5	50.0	50.7
10.0	−35.8	19.2	−29.2	28.0	−16.8	60.0	73.5
12.9	−31.5	21.0	−30.6	30.0	−15.6	70.0	94.2
15.0	−31.2	22.0	−24.1	32.0	− 2.8	80.0	111.8
Cut 7: 80% HCOOH + 20% $H_2O \rightarrow CO(NH_2)_2$							
0.0	− 5.5	18.0	−18.2	31.0	−16.0	45.0	23.5
5.0	− 6.8	23.0	−14.9	33.0	−10.1	60.0	66.0
10.0	−14.2	25.0	−14.0	35.0	− 8.0	70.0	88.0
14.0	−21.6	28.0	−14.0	40.0	− 3.7	80.0	108.2

TABLE 5

Temperatures of Crystallization of Mixtures of the Ternary System Water-Urea-Formic Acid in Sections Extending to the Water Corner

Mole % water	Temperature	Mole % water	Temperature	Mole % water	Temperature	Mole % water	Temperature
Cut 8: 5% $CO(NH_2)_2$ + 95% HCOOH → H_2O							
0.0	− 3.0°	30.5	−15.3°	53.4	−42.0°	60.0	−42.8°
15.0	− 5.0	40.0	−25.5	56.4	−47.5	72.0	−27.7
20.0	− 7.6	50.0	−38.0	58.0	−47.0	90.0	− 8.7
Cut 9: 12% $CO(NH_2)_2$ + 88% HCOOH → H_2O							
0	− 5.4	46.1	−41.0	55.8	−49.8	70.0	−27.5
17.9	−13.5	50.8	−45.0	58.0	−42.0	80.0	−17.4
30.2	−23.5	53.0	−48.2	60.1	−38.2	90.0	− 9.0
Cut 10: 25% $CO(NH_2)_2$ + 75% HCOOH → H_2O							
0.0	−13.4	26.0	−20.8	45.0	−32.2	64.5	−27.7
15.0	−16.0	30.0	−22.5	54.0	−39.5	70.0	−23.3
20.5	−18.4	35.7	−25.6	55.0	−36.5	80.0	−14.9
Cut 11: 33.3% $CO(NH_2)_2$ + 66.7% HCOOH → H_2O							
0.0	−11.5	30.4	−22.5	48.2	−34.5	60.0	−29.0
14.6	−13.9	36.4	−26.7	50.3	−37.0	70.0	−21.7
20.8	−17.0	39.0	−28.0	53.1	−34.0	75.0	−17.5
25.3	−19.8	46.0	−33.5	58.1	−30.5	85.0	−11.4
Cut 12: 35% $CO(NH_2)_2$ + 65% HCOOH → H_2O							
0.0	−15.5	27.0	−21.0	44.0	−34.0	58.0	−30.5
10.0	−16.2	35.0	−24.5	48.6	−39.2	65.0	−24.8
22.7	−18.2	42.0	−31.7	50.0	−37.5	80.0	−13.8
Cut 13: 37% $CO(NH_2)_2$ + 63% HCOOH → H_2O							
0.0	−12.5	43.0	−27.5	50.5	−32.7	60.0	−27.0
22.1	−17.7	45.0	−29.5	52.0	−32.5	70.0	−19.7
30.0	−20.0	49.0	−32.3	55.0	−30.8	80.0	−13.0

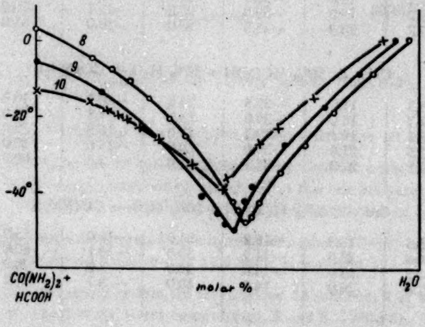

Fig. 5. Fusion diagram of the ternary system (Cuts 8-10).

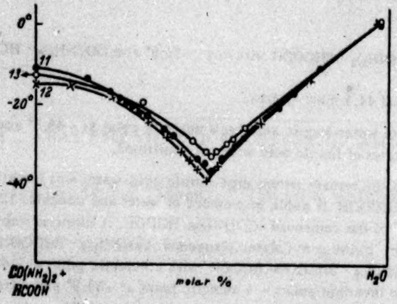

Fig. 6. Fusibility diagram of the ternary system (Cuts 11-13).

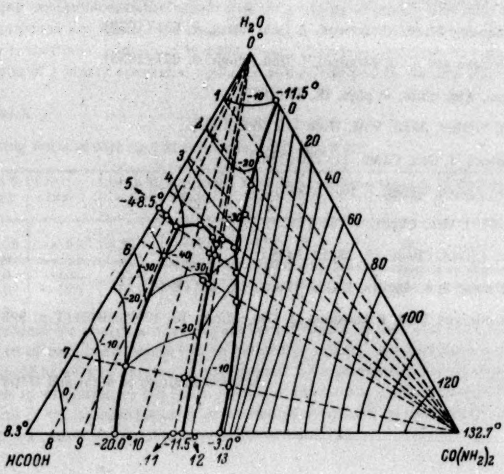

Fig. 7. Projection of the spatial phase diagram on the triangle of composition of the system HCOOH–CO(NH$_2$)$_2$–H$_2$O.

Section 11 corresponds to a binary eutectic system with a eutectic point at –37.0° and 50.3% water. It divides the diagram into two ternary systems: H$_2$O –HCOOH–CO(NH$_2$)$_2$ · 2HCOOH and H$_2$O–CO(NH$_2$)$_2$–CO(NH$_2$)$_2$ · 2HCOOH.

In the first system we have a ternary eutectic point at –49.8° and the composition: 5.5% urea, 39.25% acid and 55.25% water; the second has a eutectic point at –39.2° and the composition: 18.0% urea, 33.4% acid and 48.6% water, and a transition point at –32.2° and the composition: 22.0% urea, 28.9% acid and 49.1% water.

On the projection of the phase diagram the fields of crystallization occupy the following proportions of the total area of the triangle of the ternary system (in %): H$_2$O 12.5, HCOOH 12.2, CO(NH$_2$)$_2$ 51.0, CO(NH$_2$)$_2$ · · 2HCOOH 15.9, CO(NH$_2$)$_2$ · HCOOH 8.4.

SUMMARY

1. A fresh investigation was made of the system urea-formic acid by the method of thermal analysis. Two compounds were found:

$CO(NH_2)_2 \cdot 2HCOOH$ with m.p. -11.5° and $CO(NH_2)_2 \cdot HCOOH$

with a transition point at -3° and 44.5 mole-% urea.

The diagram of the system water-formic acid has a eutectic point at - 48.5° and 59.0 mole % water. Reports [6] of the existence of two hydrates of formic acid were not confirmed.

3. The fusion diagram of the ternary system urea-formic acid-water was investigated. It was found that a) the compound $CO(NH_2)_2 \cdot 2HCOOH$ is stable in presence of water and occupies 15.7% of the area of the diagram of the ternary system; b) the compound $CO(NH_2)_2 . HCOOH$ is likewise stable to water and occupies 8.4% of the area of the diagram; c) the cut of water-compound $CO(NH_2)_2 \cdot 2HCOOH$ divides the diagram into two ternary systems: $H_2O-CO(NH_2)_2 \cdot 2HCOOH-HCOOH$, with a eutectic point at -49.8°, and $H_2O-CO(NH_2)_2 \cdot 2HCOOH-CO(NH_2)_2$ with two invariant points - a eutectic point at -39.2° and a transition point at -32.2°.

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Received May 11, 1955

Moscow Institute of Meat and Dairy Technology

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*T.p. = C. B. Translation pagination.

PHYSICOCHEMICAL ANALYSIS OF THE REACTION OF AMINES WITH ACIDS

IV. THERMAL ANALYSIS OF THE TERNARY SYSTEM UREA-WATER-BUTYRIC ACID

M. N. Kuznetsova and A. G. Bergman

Our systematic investigations of binary systems of urea with a series of aliphatic acids by the method of thermal analysis have shown that only the first three members of the homologous series of fatty acids, namely formic, acetic and propionic acids, give crystallizable compounds with urea [1]. Urea usually behaves like a monoacidic base, forming equimolecular compounds with the majority of acids. With fatty acids, however, another type of urea compound was found: one molecule of urea with two molecules of acid. One possible reason for this behavior is that urea, containing two NH_2 groups, functions sometimes as a diacidic base; another possibility is that addition of a binary associated molecule of the fatty acid to the urea takes place.

TABLE 1

Melting Point of Mixtures of n-Butyric Acid with Water

Mole % water	Temper-ature	Mole % water	Temper-ature	Mole % water	Temper-ature	Mole % water	Temper-ature
0.04	— 8.3°	30.0	—11.8°	41.0	—7.7°	70.0	—2.7°
10.0	— 9.3	32.5	—12.5	45.0	—5.8	80.0	—2.5
15.0	—10.0	35.0	—11.0	50.0	—5.0	90.0	—2.0
20.0	—10.3	37.0	— 9.2	60.0	—3.5	100	0.0

To clarify this problem we resolved to investigate the interaction of urea with acids in presence of water. The degree of association of associated liquids can be reduced by mixing. It might have been expected that in aqueous solutions we should be able to detect the more normal 1:1 type of compound of urea with fatty acids. However, in our previous investigation by the fusion method of the ternary system water-urea-acetic acid, we did not obtain indications of the crystallization of an equimolar compound; on the contrary, the compound $CO(NH_2)_2 \cdot 2CH_3COOH$ was found to be stable in presence of water [2].

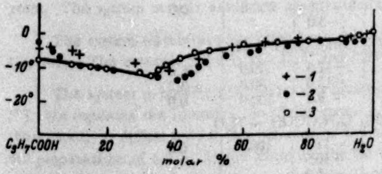

Fig. 1. Fusibility diagram of the system butyric acid-water. 1) Ballo's data [6]; 2) Faucon's data; 3) our data.

TABLE 2

Position of Eutectic Point of the System Water-n-Butyric Acid According to the Data of Various Authors

Melting point of preparation of the acid	Mole% water in eutectic mixture	Melting point of eutectic mixture	Author
—3.12°	40.86	—13.4°	[2]
—4.50	37.86	—10.4	[6]
—8.0	32.5	—12.5	[1, 2]

TABLE 3

Temperature of Crystallization of Mixtures of the Ternary System Water-Urea-n-Butyric Acid in Sections Extending to the Urea Corner

Mole % urea	Temperature	Mole % urea	Temperature	Mole % urea	Temperature	Mole % urea	Temperature
Cut 1: 50% $C_3H_7COOH + 50\% H_2O \rightarrow CO(NH_2)_2$							
0.0	−4.9°	15.0	−14.5°	30.0	36.0°	60.0	99.3°
5.0	−6.1	20.0	+5.8	40.0	64.3	70.0	110.0
10.0	−8.2	25.0	22.0	50.0	82.5	80.0	119.0
Cut 2: 59% $C_3H_7COOH + 41\% H_2O \rightarrow CO(NH_2)_2$							
0.0	−7.8	16.0	−16.7	30.0	40.4	60.0	100.3
10.0	−12.8	18.0	−11.0	40.0	67.0	70.0	111.2
14.0	−16.0	20.0	+8.0	50.0	85.8	80.0	119.5
Cut 3: 67.5% $C_3H_7COOH + 32.5\% H_2O \rightarrow CO(NH_2)_2$							
0.0	−12.5	18.0	−23.5	30.0	40.2	70.0	112.0
10.0	−18.0	20.0	−7.5	40.0	67.3	80.0	120.5
16.0	−22.5	25.0	27.5	50.0	86.5	100.0	132.7
Cut 4: 75% $C_3H_7COOH + 25\% H_2O \rightarrow CO(NH_2)_2$							
0.0	−11.4	15.0	−21.5	35.0	55.0	70.0	113.0
5.0	−13.7	20.0	1.0	45.0	78.5	80.0	121.2
10.0	−17.7	25.0	25.4	60.0	103.3	100.0	132.7

TABLE 4

Temperature of Crystallization of Mixtures of the Ternary System Water-Urea-n-Butyric Acid in Sections Extending to the Water Corner

Mole % water	Temperature	Mole % water	Temperature	Mole % water	Temperature	Mole % water	Temperature
Cut 5: 10% $CO(NH_2)_2 + 90\% C_3H_7COOH \rightarrow H_2O$							
0.0	−14.5	28.0	−16.3	36.0	−12.4	70.0	−2.7
10.0	−15.4	30.0	−16.5	50.0	−5.5	80.0	−2.5
20.0	−16.3	32.0	−15.2	60.0	−3.0	100.0	0.0
Cut 6: 15% $CO(NH_2)_2 + 85\% C_3H_7COOH \rightarrow H_2O$							
0.0	−18.0	25.0	−19.2	35.0	−8.5	85.0	−2.3
10.0	−18.2	28.0	−19.5	55.0	−4.8	100.0	−0.0
20.0	−18.5	34.0	−13.3	75.0	−2.8		
Cut 7: 18% $CO(NH_2)_2 + 82\% C_3H_7COOH \rightarrow H_2O$							
0.0	−18.9	25.0	−20.5	36.0	−14.6	70.0	−3.8
10.0	−19.0	28.0	−21.6	50.0	−7.0	80.0	−3.0
20.0	−19.4	32.0	−17.7	60.0	−4.5	100.0	0.0
Cut 8: 21% $CO(NH_2)_2 + 79\% C_3H_7COOH \rightarrow H_2O$							
0.0	−10.0	25.0	−25.0	36.0	−15.4	80.0	−1.4
10.0	−14.2	28.0	−22.3	50.0	−7.5	100.0	0.0
18.0	−18.2	30.0	−19.8	70.0	−3.0		
Cut 9: 30% $CO(NH_2)_2 + 70\% C_3H_7COOH \rightarrow H_2O$							
0.0	41.5	33.0	7.7	49.0	−12.5	70.0	−5.0
10.0	31.6	42.0	−1.5	52.0	−11.0	80.0	−3.2
22.0	20.0	47.0	−9.0	59.0	−9.4	100.0	0.0
Cut 10: 50% $CO(NH_2)_2 + 50\% C_3H_7COOH \rightarrow H_2O$							
0.0	92.5	50.0	20.0	72.4	−11.9	100.0	0.0
20.0	65.8	60.0	5.3	75.0	−10.5		
35.0	43.2	70.0	−9.5	85.0	−6.0		

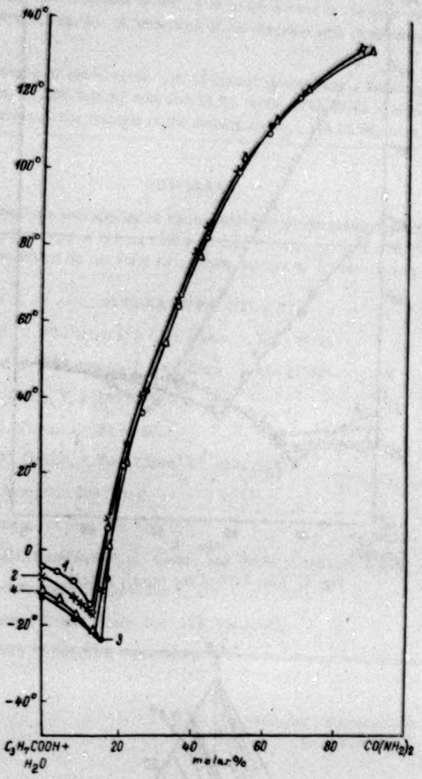

Fig. 2. Cuts 1-4 of the ternary system.

In this paper we present data for the fusibility of the ternary system water-urea-n-butyric acid. The procedure was described previously [1, 2]. All compositions are expressed in molar percentages. All the three binary systems were previously investigated and are represented by the simplest type of diagrams with a eutectic point. The system butyric acid-urea has a eutectic point at −18.9° and 18.0 % urea [1].

The system water-urea has often been studied [3-5]. Our data confirm the results of the preceding investigations. The eutectic point is at −11.5° and 12.7% urea.

The system n-butyric acid-water was investigated by the fusion method by Ballo [6] and by M. A. Faucon [7]. We repeated the investigation of this system. The plotted diagram is essentially similar to that of the authors cited; it differs only in the constants of the eutectic point, and this may be attributed to the use of different preparations of acids. In the literature the melting point of n-butyric acid is given as −7.9° [8], −3.12° [9], −4.70° [10] and −8.0° [11]. Our preparation (pure for analysis) was purified by distillation and had m.p. −8.0°. Data for the investigation of this system are set forth in Table 1 and plotted in Fig. 1. The data of [6,7] are shown on the same diagram for comparison. In Table 2 are set forth the comparative data for the position of the eutectic point in this system as determined by various authors. The melting points of the acids used by these authors are also given.

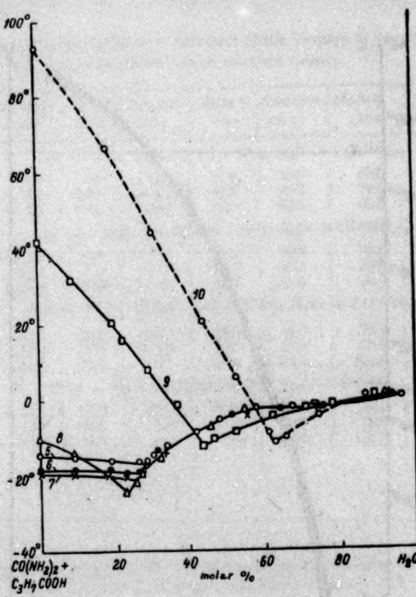

Fig. 3. Cuts 5-10 of the ternary system.

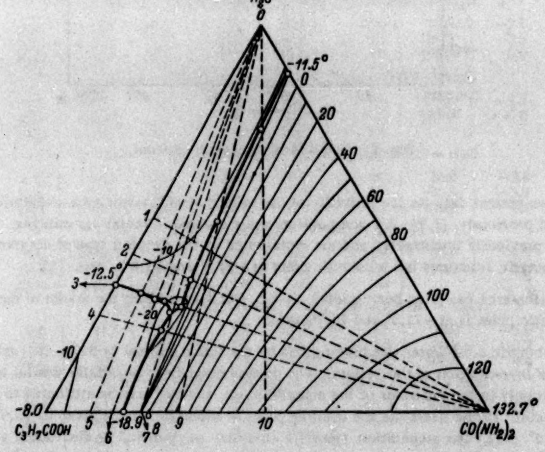
H₂O
0
-11.5°
0
20
40
60
80
100
120
132.7°
1
2
-10
-12.5°
3
4
-20
-10
-8.0
C₃H₇COOH
5
6
-18.9
7
8
9
10
CO(NH₂)₂

Fig. 4. Fusibility diagram of the system water-urea-n-butyric acid.

We investigated 10 sections in the ternary system, 4 of which extend to the urea corner (Table 3, Fig. 2) and 6 to the water corner (Table 4, Fig. 3). A projection of the diagram with isotherms at 10° intervals was also plotted (Fig. 4).

The diagram is characteristic of the simplest type of ternary system with a eutectic point at −25.0° and the composition of 15.75% urea, 59.25% butyric acid and 25.0% water. The fields of crystallization of the components occupy the following areas of the triangle of the ternary system: ice 18.6%, urea 71.0%, butyric acid 10.4%.

SUMMARY

The method of thermal analysis was applied in an investigation of the ternary system water-urea-n-butyric acid, which constitutes the simplest type of system with a ternary eutectic point at −25.0°. Consequently, urea and n-butyric acid in aqueous solutions do not form compounds capable of crystallization.

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Received May 11, 1955

Moscow Institute of the Meat and
Dairy Industry

DIELECTRIC PROPERTIES OF SOLUTIONS OF ALUMINUM BROMIDE IN SOME ORGANIC SUBSTANCES

I. A. Sheka

The present communication contains the results of an investigation of the processes of complex formation in systems formed by aluminum bromide with organic substances in solvents which are inert to them. The investigation was conducted by the method of physicochemical analysis of the solutions with use of the dielectric constant and the polarization as characteristic properties. We had previously shown [1] that a special feature of this method is the detection of a new coordinative bond which is developed by complex formation between reacting molecules. The coordinative bond being, to a greater or lesser degree, polar, increases the dielectric polarization of the complex in comparision with the polarization of the component molecules, and this is accompanied by an increase in the dielectric constant of the solution. Since the polarization is an additive property the concentration of the complex formed can be evaluated from the magnitude of the deviations of the polarization or of the dielectric constants, from the values calculated according to the mixing law.

The method in question had already been applied by us to the detection of intermolecular interaction in systems formed by allyl mustard oil with amines; some of these systems exhibit definite chemical interaction, while others do not interact [2]. The objective of the present investigation was to ascertain the possibility of applying the proposed method to the investigation of processes of complex formation in systems consisting of aluminum bromide and some organic substances.

The following considerations induced us to choose aluminum bromide and various organic substances as materials for the present investigation:

1. Aluminum halides form numerous complex compounds with diverse organic substances. The existence of these compounds is confirmed with the help of thermal analysis. Many of them are isolated in the form of crystals. The majority of the compounds formed by aluminum halides with organic substances containing oxygen nitrogen and sulfur are stable. On the phase diagrams they are represented by well-defined dystectics of equimolar composition. The heat of formation of this type of compound is often very high [3]. In the light of these observations there is reason to believe that compounds of this type exist or are formed also in solutions.

2. Due to the interaction with organic substances with widely differing properties, the molecular compounds of halides of aluminum vary in stability, ranging from those whose formation is accompanied by a high thermal effect to those which are unstable and whose existence is only possible under special conditions. The investigation of such systems is of great interest since the deviations of their polarization must vary. Apart from that aluminum and its complex compounds are readily soluble in a series of nonpolar solvents, and this facilitates the performance of the investigation.

3. Halides of aluminum and their molecular compounds are also of practical interest since some of them are extensively used in organic synthesis as catalysts.

We investigated the processes of complex formation in these systems by the method of isomolar concentrations of Ostromyslensky and Job as well as by the method of maintaining constant concentration in solution of one of the reactants while the concentration of the second component was varied.

Study of the Dielectric Properties of Solutions by the Method of Isomolar Concentrations

In this part of the work we studied systems formed by aluminum bromide with diethyl and diphenyl ethers, benzophenone, anisole and pyridine. With these substances, aluminum bromide forms complex compounds some of which are isolated in the crystalline state; their composition in solution was not studied.

The following procedure was used. The dielectric constants of solutions prepared by the method of isomolar concentrations were determined. Measurements were made by the beat method at a wavelength of 301.3 m. The data obtained served as a basis for calculation of the polarization of the reacting components; for the ternary system this was effected with a formula based on the mixing law and on the Clausius-Mosotti equation:

$$P_2 = \frac{1000}{n}\left[\frac{\epsilon - 1}{\epsilon + 2} - Kd\right] + K\left[aM_1 + bM_2\right],$$

where n is the molarity of the solution; ϵ and d are the dielectric constant and the density of the solution; $K = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \cdot \frac{1}{d_0}$ is the specific dielectrical polarization of the solvent; M_1 and M_2 are the molecular weights of the dissolved substances, a and b are the molar proportions of components in solution (their sum equals unity).

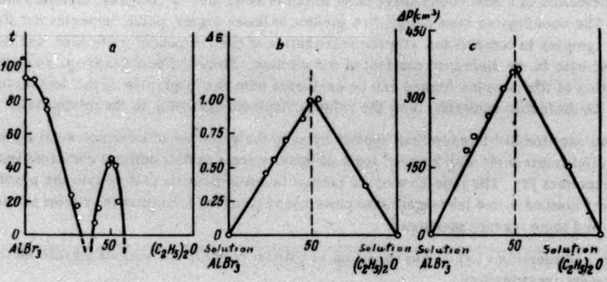

Fig. 1. Aluminum bromide-diethyl ether in carbon disulfide. a) melting point diagram of the system $AlBr_3$-$(C_2H_5)_2O$ according to Plotnikov and Kaplan [8]; b) Δε/composition diagram; c) ΔP/composition diagram.

TABLE 1

Dielectric Constants and Polarization of the System $AlBr_3$-$(C_2H_5)_2O$ in Carbon Disulfide at 20° (concentration of starting solutions 0.306 M)

Ratio of volumes $\frac{V_{AlBr_3}}{V_{(C_2H_5)_2O}}$	ϵ_{exptl}	Δε	d	P2 exptl (cm³)	ΔP(cm³)
10 : 0	2.680	0	1.3135	46.8	0
7.8 : 2.2	3.136	0.460	1.2985	234.6	186.0
7.3 : 2.7	3.218	0.543	1.2955	265.0	216.0
6.6 : 3.4	3.361	0.688	1.2903	315.7	266.1
5.7 : 4.3	3.529	0.857	1.2844	372.0	321.8
5.1 : 4.9	3.652	0.981	1.2802	411.1	360.4
4.6 : 5.4	3.673	1.003	1.2773	417.8	366.7
1.9 : 8.1	3.045	0.365	1.2587	204.9	151.7
0 : 10	2.680	0	1.2460	54.7	0

TABLE 2

Dielectric Constants and Polarization of the System $AlBr_3$–$(C_6H_5)_2O$ in Carbon Disulfide at 20° (concentration of original solution 0.204 M)

Ratio of volumes $\frac{V_{AlBr_3}}{V_{(C_6H_5)_2O}}$	ϵ_{exptl}	$\Delta\epsilon$	d	P2 exptl (cm^3)	$\Delta P(cm^3)$
10 : 0	2.662	0	1.2959	45.0	0
9.1 : 0.9	2.759	0.096	1.2932	110.9	63.7
8.4 : 1.6	2.863	0.199	1.2903	178.8	129.1
7.9 : 2.1	2.911	0.247	1.2884	209.5	158.3
6.5 : 3.5	3.085	0.419	1.2832	315.3	259.7
5.2 : 4.8	3.225	0.558	1.2786	395.6	336.2
5.0 : 5.0	3.241	0.573	1.2778	404.7	344.6
3.7 : 6.3	3.105	0.436	1.2735	332.5	268.8
3.2 : 6.8	3.045	0.377	1.2718	300.4	235.2
2.3 : 7.7	2.939	0.268	1.2683	238.9	170.8
0.9 : 9.1	2.782	0.110	1.2635	144.1	72.0
0 : 10	2.674	0	1.2603	74.9	0

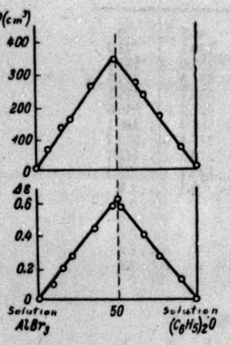

Fig. 2. Aluminum bromide-diphenyl ether in carbon disulfide.

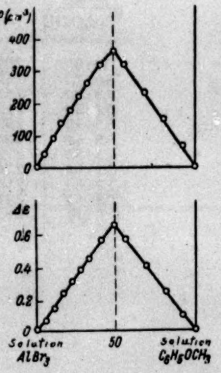

Fig. 3. Aluminum bromide-anisole in benzene.

System Aluminum Bromide-Diethyl Ether in Carbon Disulfide

Reference to the formation of a compound of aluminum bromide with diethyl ether is made by Nickles [4] and by Menshutkin [5]. Later, V. A. Plotnikov [6,7] made a closer study and isolated the complex compound of aluminum bromide with diethyl ether in the form of lustrous crystals with m.p. 47°. Plotnikov and Kaplan [8] partly investigated the fusibility of the system aluminum bromide-ether (in the concentration range 5.21 to 29.1 mole % and 41.6 to 54.6 mole % ether) and found that a dystectic appeared on the phase diagram corresponding to $AlBr_3(C_2H_5)_2O$ (Fig. 1).

We studied the dielectric constants and the polarization of the system $AlBr_3$–$(C_2H_5)_2O$ in carbon disulfide solution. Data are presented in Table 1 and Fig. 1.

The $\Delta\epsilon$/composition and ΔP/composition diagrams show that the maxima of deviations of the dielectric constants and the polarization from additivity correspond to equimolecular compounds of aluminum bromide and ether, i.e., that these solutions contain a complex of the same composition as in the absence of a solvent.

System Aluminum Bromide-Diphenyl Ether in Carbon Disulfide

Aluminum bromide and diphenyl ether form a compound $AlBr_3 \cdot (C_6H_5)_2O$ [9] crystallizing from benzene or carbon disulfide solution in the form of pale-yellow plates with m.p. 127°.

Results of the investigation of the dielectric constants and polarization of the system $AlBr_3-(C_6H_5)_2O$ in carbon disulfide are presented in Table 2 and Fig. 2.

The sharply defined maxima of deviations on the Δε /composition and ΔP/composition diagrams, corresponding to a 1:1 ratio of components, indicate formation in solution of the compound $AlBr_3 \cdot (C_6H_5)_2O$, in agreement with the literature data cited above.

We also investigated the same system in benzene at various temperatures. The results showed that in the 0.1 to 1 M range of concentrations, the maxima of the deviations of the dielectric constants and dielectric polarization from additivity correspond to equimolecular composition of the complex.

TABLE 3

Dielectric Constants and Dielectric Polarization of the System $AlBr_3-(C_6H_5)_2O$ in Carbon Disulfide at 20° (concentration of original solutions 0.204 M).

Ratio of volumes $\frac{V_{AlBr_3}}{V_{C_6H_5OCH_3}}$	ϵ_{exptl}	Δε	d	P2 exptl (cm³)	ΔP(cm³)
10 : 0	2.365	0	0.9250	80.5	0
8.9 : 1.1	2.517	0.155	0.9204	170.5	92.7
7.8 : 2.2	2.673	0.313	0.9156	257.0	181.9
6.6 : 3.4	2.829	0.472	0.9108	337.8	265.5
5.9 : 4.1	2.926	0.570	0.9076	385.7	315.1
5.0 : 5.0	3.009	0.655	0.9036	425.2	356.8
4.3 : 5.7	2.924	0.572	0.9010	384.9	318.1
3.1 : 6.9	2.748	0.399	0.8956	397.4	233.7
1.9 : 8.1	2.585	0.238	0.8904	210.5	149.7
0.8 : 9.2	2.443	0.099	0.8858	129.7	71.4
0 : 10	2.343	0	0.8823	56.3	0

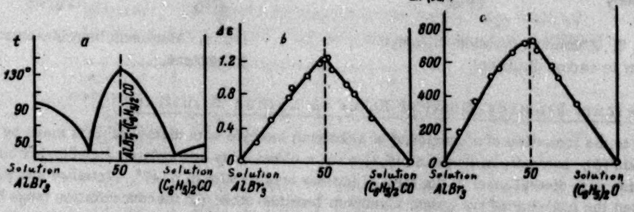

Fig. 4. Aluminum bromide-benzophenone in benzene.
a) Fusibility diagram of the system $AlBr_3-(C_6H_5)_2CO$ according to B. N. Menshutkin [12],
b) Δε /composition diagram, c) ΔP /composition diagram.

System Aluminum Bromide-Anisole in Benzene

The complex $AlBr_3 \cdot C_6H_5OCH_3$ has been isolated in the crystalline state [9]. Our data for the deviations of the dielectric constants and polarization from the additive value testify to the formation of this compound in benzene solution.

Results of determination of the dielectric constants and dielectric polarization of the system aluminum bromide-anisole are presented in Table 3 and Fig. 3.

System Aluminum Bromide-Benzophenone in Benzene

On the basis of ebullioscopic investigations, Kohler [11] reported the existence of a complex compound of aluminum bromide with benzophenone. By thermal analysis of the system $AlBr_3-(C_6H_5)_2CO$, B. N. Menshutkin [12] detected on the phase diagram a dystectic with the composition $AlBr_3 \cdot (C_6H_5)_2CO$, and he isolated a compound of aluminum bromide with benzophenone in the form of long yellow plates with m.p. 142°.

Our investigations of the dielectric properties of the system $AlBr_3-(C_6H_5)_2CO$ in benzene (Table 4 and Fig. 4) show that the maxima of the deviations of the dielectric constants and the dielectric polarization coincide with the position of the dystectic on the fusion curve and correspond to the compound $AlBr_3 \cdot (C_6H_5)_2CO$.

TABLE 4

Dielectric Constants and Dielectric Polarization of the System $AlBr_3-(C_6H_5)_2CO$ in Benzene (concentration of starting solutions 0.2016 M)

Ratio of volumes $\frac{V_{AlBr_3}}{V_{benzophenone}}$	ϵ_{exptl}	$\Delta\epsilon$	d	P2 exptl (cm³)	ΔP (cm³)
10 : 0	2.355	0	0.9152	86.8	0
9.1 : 0.9	2.627	0.257	0.9126	289.0	189.8
8.1 : 1.9	2.915	0.529	0.9100	479.1	366.0
7.2 : 2.8	3.177	0.776	0.9074	634.0	507.6
5.9 : 4.1	3.478	1.056	0.9040	794.1	649.7
5.0 : 5.0	3.649	1.212	0.9016	877.8	720.8
4.5 : 5.5	3.554	1.109	0.9002	833.7	669.6
3.8 : 6.2	3.392	0.934	0.8981	754.5	579.5
3.3 : 6.7	3.283	0.817	0.8968	698.4	516.4
2.2 : 7.8	3.031	0.546	0.8973	559.2	360.9
0 : 10	2.521	0	0.8879	229.2	0

System Aluminum Bromide-Pyridine in Benzene

According to I. Kablukov and A. Sakhanov [13], aluminum bromide and pyridine form a compound $AlBr_3 \cdot 2C_5H_5N$. V. A. Plotnikov and S. S. Balyasny [14], who investigated the same system by the method of thermal analysis, indicate the formation of the following compounds: $AlBr_3 \cdot C_5H_5N$, $Al_2BR_6 \cdot C_5H_5N$, and $2Al_2Br_6 \cdot 3C_5H_5N$.

Our observations of the deviation of the dielectric constants and the dielectric polarization in the system aluminum bromide-pyridine in benzene pointed to the existence of only one compound – $AlBr_3 \cdot C_5H_5N$ (Table 5, Fig. 5).

It is possible that some of the compounds of aluminum bromide with pyridine reported in the literature in the absence of solvent or in presence of excess of one of the components are formed by weak forces of polarized interaction of pyridine or aluminum bromide with the strongly polar molecule of $AlBr_3 \cdot C_5H_5N$ (the dipole moment according to our measurements is 8.19 D). These compounds break down in solution, and therefore only the most stable compound $AlBr_3 \cdot C_5H_5N$ is detected on the $\Delta\epsilon$/composition and ΔP/composition curves.

The foregoing examples confirm our hypothesis that if there is interaction between the components of a solution bound up with formation of a new coordinate bond, then this will be manifested by a rise in the dielectric

TABLE 5

Dielectric Constants and Dielectric Polarization of the System $AlBr_3-C_5H_5N$ in Benzene at 25° (concentration of starting solutions 0.1337 M)

Ratio of volumes V_{AlBr_3} / $V_{pyridine}$	ϵ_{exptl}	$\Delta\epsilon$	d	P2 exptl (cm^3)	ΔP (cm^3)
10 : 0	2.343	0	0.8975	118.1	0
9.1 : 0.9	2.447	0.105	0.8953	238.6	122.1
8.1 : 1.9	2.552	0.211	0.8933	354.1	239.1
7.2 : 2.8	2.653	0.313	0.8911	460.6	347.2
6.3 : 3.7	2.752	0.412	0.8891	560.2	448.4
5.0 : 5.0	2.859	0.520	0.8862	663.3	553.6
3.8 : 6.2	2.753	0.415	0.8837	559.6	451.7
3.2 : 6.8	2.675	0.338	0.8822	480.2	373.5
1.5 : 8.5	2.469	0.133	0.8785	257.7	153.8
0.3 : 9.7	2.378	0.043	0.8757	152.7	50.8
0 : 10	2.335	0	0.8752	101.4	0

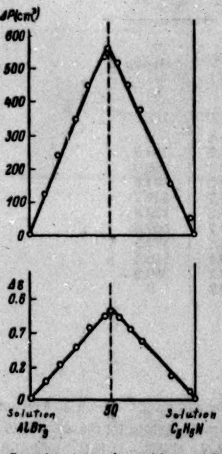

Fig. 5. Aluminum bromide-pyridine in benzene.

constants and dielectric polarization of the solutions. Furthermore, by the examples of the system aluminum bromide-pyridine and the (previously partly studied) system with dioxane [1], it was shown that compounds of the solvated type, formed by inductive reaction (van der Waals forces) are not reflected on the $\Delta\epsilon$/composition and ΔP/composition curves due to their instability in solutions.

The systems here considered contain stable compounds, isolated in crystalline form or demonstrated by thermal analysis; their formation is accompanied by an exothermic thermal effect. The $\Delta\epsilon$/composition and ΔP/composition diagrams are made up of two straight lines which intersect at a singular point corresponding to the composition of the compound. The maximum of the deviations of polarization reach very high values (350-700 cm^3).

Aluminum bromide also forms unstable compounds with some organic substances. A possible example is the system $AlBr_3-C_2H_5Br$. The study of the electrochemical [15-17] and catalytic properties [18-20] of the molecular state in solutions [21] and of the light absorption in the ultraviolet portion of the spectrum [22,23] led investigators to the conclusion that interaction takes place between aluminum bromide and ethyl bromide. By examination of the dielectric properties of solutions of $AlBr_3$ and C_2H_5Br in carbon disulfide, we demonstrated, jointly with Z. A. Sheka [24], the formation of the compound $AlBr_3 \cdot C_2H_5Br$, and this was later confirmed by thermal analysis. The low heat of solvation of aluminum bromide by ethyl bromide (3.65 kcal/mole) is evidence of the low stability of the compound $AlBr_3 \cdot \cdot C_2H_5Br$ [25]. In harmony with these observations, the diagrams of deviation of the dielectric constants and polarization of this system in carbon disulfide contain a maximum with a deviation of polarization of $\Delta P = 42.8$ cm^3, i.e. many times smaller than for stable compounds.

Consequently, the method of determination of the polarization and dielectric constants enables us, with the help of the form of the diagrams and the magnitude of the deviation of polarization, not only to demonstrate the existence of compounds formed in solutions, but also to determine their relative stability.

Investigation of Complex Formation with Constant Concentration of One of the Reacting Components

In the physicochemical investigation of solutions of isomolar concentration by the Ostromyslensky-Job method, the maxima or minima on the composition/property diagram usually reflect the composition of the compound predominating in the given system. Formation of other, less stable, compounds cannot always be established by this method. In this connection it is sometimes possible to obtain more reliable results by studying systems with constant concentration of one of the components in the solution and variable concentration of the other.

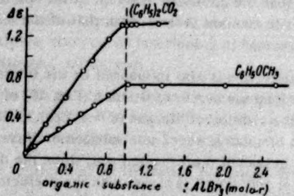

Fig. 6. Systems of aluminum bromide with anisole and benzophenone in benzene.

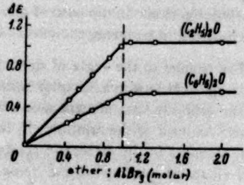

Fig. 7. Systems aluminum bromide with diphenyl and diethyl ethers in carbon disulfide.

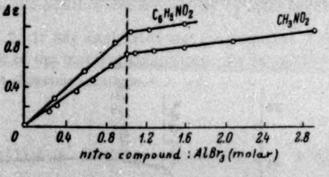

Fig. 8. Systems aluminum bromide with nitrobenzene (in carbon disulfide) and nitromethane (in benzene).

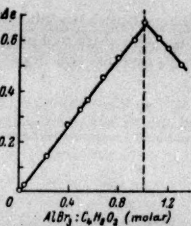

Fig. 9. Aluminum bromide-dioxane in benzene.

It appeared expedient to investigate the dielectric properties of systems aluminum bromide-organic substances-solvent with constant concentration of one of the reacting substances with the objective of verifying the suitability of this method for investigation of solutions. For this purpose a solution was prepared of aluminum bromide or organic substance in benzene, carbon disulfide or some other solvent indifferent to the given substances. After measuring the dielectric constant of the solution, the second component was introduced in small portions and the dielectric constants were again measured.

Results of the investigations, in the form of titration curves, are presented in Figs. 6-11. On the abscissas are plotted the molar ratios of reacting substances, and on the ordinates, Δε, the difference between the dielectric constants of the solution and the pure solvent.

With the objective of clarifying the possibility of formation in solutions of compounds with other than equimolar ratios of components, the majority of the investigations were carried out both with constant concentration of aluminum bromide in solution and with constant concentration of the organic substance.

The diagrams obtained may be arranged in two groups.

1) Diagrams with one inflection. In this case, the curve rises at the start of titration due to formation in the solution of a complex compound with a new coordinate bond, which is manifested by a rise in the dielectric constant of the solution. After completion of the reaction, further addition of an excess of one of the components is accompanied by a more or less sharp inflection in the curve which may then run parallel to the abscissas, as, for example, in Figs. 6 and 7 for the systems aluminum bromide with anisole and benzophenone in benzene, aluminum bromide with diethyl ether and diphenyl ether in carbon disulfide; in other cases, the curve rises gradually as in Fig. 8 (aluminum bromide with nitromethane and nitrobenzene), or a maximum is formed (system aluminum bromide-dioxane in benzene, Fig. 9).

The character of the change of the dielectric constants of the solutions after inflection in dependence on the concentration of the second component is bound up with the value of the dielectric constant of the latter. If the dielectric constant of the added substance is greater than the dielectric constant of the solution, the curve rises after inflection. In the case of dioxane, whose dielectric constant is lower than that of the solution of aluminum bromide in benzene, the curve falls after the maximum.

The change in the angle of slope of the curve after inflection is also influenced by the interaction of the added component with the complex formed. Thus, we see from the curves of titration (Fig. 10) of a solution of aluminum bromide with dioxane that after the maximum the addition of dioxane (ϵ = 2.218) hardly changes the dielectric constant of the solution. If, however, aluminum bromide is added to a solution of dioxane in benzene, a fall is observed in the dielectric constant of the solution instead of the expected rise, since the dielectric constant of aluminum bromide in the liquid state (ϵ = 3.375 at 100° [26]) is higher than the dielectric constant of the solution (Fig. 9). The explanation is that after the maximum, corresponding to the compound $AlBr_3 \cdot C_4H_8O_2$, addition of aluminum bromide leads to formation of a second complex $Al_2Br_6 \cdot C_4H_8O_2$, whose dipole moment is lower than the first

$$(\mu_{Al_2Br_6 \cdot C_4H_8O_2} \doteq 4.62\,D, \quad \mu_{AlBr_3 \cdot C_4H_8O_2} = 5.23\,D).$$

2) Diagrams with two inflections are observed in the systems aluminum bromide-dioxane in benzene and toluene (Fig. 10). At the start of titration of the solutions of aluminum bromide with dioxane, the dielectric constant of the solutions falls slightly and then rises sharply to a maximum at an aluminum bromide/dioxane ratio of 2:1.

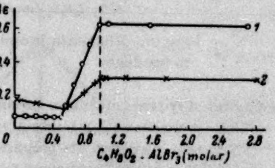

Fig. 10. Systems aluminum bromide-dioxane in benzene (1) and toluene (2).

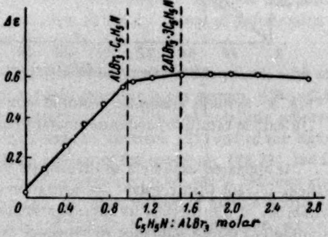

Fig. 11. Aluminum bromide-pyridine in benzene.

The first inflection corresponds to the complex $Al_2Br_6 \cdot C_4H_8O_2$, and the second to the complex $AlBr_3 \cdot C_4H_8O_2$; we isolated both compounds in the crystalline form in collaboration with K. F. Karlysheva [27]. The fall in dielectric constant, reflected in the first part of the curves of Fig. 10, is evidently associated with low solubility of the complex $Al_2Br_6 \cdot C_4H_8O_2$ in benzene and toluene and with its partial separation from solution. Further addition of dioxane leads to formation of the more soluble compound $AlBr_3 \cdot C_4H_8O_2$ to which corresponds the maximum on the curves.

Ya. F. Mezhenny [28] also reports the formation of a third compound with the composition $AlBr_3 \cdot 2C_4H_8O_2$, but this is not reflected on the curves; apparently this compound is unstable in solutions and exists only in the crystalline state. A second example of this type of diagram is that of the system $AlBr_3$–pyridine in benzene (Fig. 11). Two inflections are observed on the curve when pyridine is added to a solution of aluminum bromide in benzene: a sharp inflection corresponding to the compound $AlBr_3 \cdot C_5H_5N$, and a weaker one evidently corresponding to the less stable $2AlBr_3 \cdot 3C_5H_5N$. We may note that only one compound $AlBr_3 \cdot C_5H_5N$ is detected by the method of isomolar concentrations in the system aluminum bromide-pyridine in benzene.

The method applied in the present paper for study of the interaction of substances in solution with the help of the dielectric constant and polarization offers the possibility of determining the molar ratios of the components entering into reaction. This may find application in titration in non-aqueous solutions and in establishing the experimental basis of theories of generalized acids and bases which have undergone much development in recent years [29-32]. In these theories great importance is attached mainly to acid-base interaction ("neutralization" reactions of aprotonic acids and bases); various compounds act as aprotonic compounds, including aluminum halides; compounds functioning as bases are organic substances containing electron-donating atoms – oxygen, nitrogen, sulfur, etc.

It remains to add that there are few reliable methods of determination of the end of titration in non-aqueous solutions which enable the establishment of quantitative ratios in neutralization of aprotonic acids and bases; consequently, the conclusions from investigations on this problem are not always well-founded.

The application for the above purpose of the method of physicochemical analysis, based on the dielectric properties of solutions, can evidently be extremely useful.

SUMMARY

1. A study was made of the dielectric properties of systems formed by aluminum bromide with anisole, pyridine, diphenyl ether, diethyl ether, benzophenone, nitromethane, nitrobenzene and dioxane, using benzene and carbon disulfide as solvents.

2. It was shown that the maxima of deviations of dielectric constants and polarization on the composition/ /property diagrams in solutions correspond to the composition of complexes obtained by preparative methods or whose composition was determined by other physicochemical methods.

3. It was established that measurement of the dielectric constants of solutions with constant concentration of one of the reacting components can be utilized as an indicator of the end of titration in acid-base interaction in non-aqueous solutions.

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Received May 19, 1955

Institute of General and Inorganic Chemistry
Academy of Sciences Ukrainian SSR

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INVESTIGATION OF THE VISCOSITY, DENSITY AND ELECTRICAL CONDUCTIVITY OF THE SYSTEM QUINOLINE-ACETIC ACID

S. P. Miskidzhyan and S. S. Kirilyuk

Although the system quinoline-acetic acid has already been studied by the methods of physicochemical analysis, the number and composition of the compounds formed between the components of the system has nevertheless not been definitely established.

Thus, for example, the phase diagram obtained by Puschin and Rikowski [1] points to the formation of one compound with the composition $CH_3COOH \cdot C_9H_7N$. On the other hand, the refractive index isotherm obtained by Puschin and Mamawulji [2] indicates the presence of a compound $C_9H_7N \cdot 2CH_3COOH$ in the system, since the maximum deviation of the refractive index from additivity corresponds to 66.6 mole % acetic acid. It is known, however, that the unsupported evidence of the refractive index diagram does not suffice for the drawing of a firm conclusion about the composition of the compound formed in the system. The isotherm of electrical conductivity of this system, obtained by Puschin and Tutundzic [3], has one maximum corresponding to 12 mole % quinoline, and is not informative about the composition of the compound formed in the system. M. A. Klochko [4] calculated the relative temperature coefficient of electrical conductivity and suggested that a special point can be obtained on the curve of the temperature coefficient of electrical conductivity which indicates the composition of the compound formed. Although such a method does, in many cases, lead to positive results, in the present case the shape of the curve is almost identical with that of the electrical conductivity isotherm, and consequently provides no new information about the composition of the compound.

The above review of previous work on the system quinoline-acetic acid justifies the conclusion that no reliable data have been published in the past about the composition of the compound formed in the liquid phase. Since this problem is of definite scientific interest, we decided to investigate the system by the viscosity and density method. Viscosity is known to be a most revealing property in physicochemical analysis for establishing the composition of a compound formed in a liquid system. In the literature we failed to find any references to these two properties of the system. Some authors, in particular Hölzl [5], M. A. Klochko [4], N. A. Izmailov [6] and others, have shown that the study of liquid binary systems in an inert solvent sometimes gives convincing data about the occurrence of interaction between the components in the liquid phase. We therefore decided to utilize the method in question for conclusive establishment of the number and composition of the compounds formed in the system under investigation by us. With this objective, we measured the specific electrical conductivity of mixtures of quinoline and acetic acid in anhydrous methyl alcohol as the inert solvent.

EXPERIMENTAL

The starting components were obtained in the following manner: quinoline, chemically pure grade, was dried over potassium hydroxide and then distilled; the fraction with b.p. 235-237° was collected. Its density was d^{20} 1.0939. Acetic acid was obtained by several freezings of glacial acetic acid followed by distillation. The freezing point of the acid obtained in this manner was 16.5°. Mixtures were made up by weight. Considerable heating was observed on mixing the components. The prepared solutions were kept in dark bottles with ground-glass stoppers which were placed in a closed, dark-colored desiccator. No outward changes were observed in these mixtures in the course of a year, whereas part of the same solutions which had not been stored in the dark desiccator acquired a reddish color, as was also noted by other authors [3].

Anhydrous methyl alcohol was obtained by the method described in the literature [7].

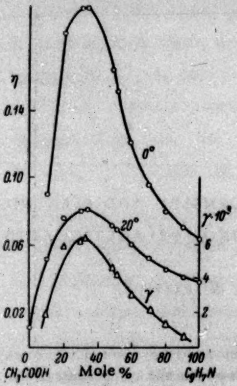

Fig. 1. Viscosity at 0 and 20° and the temperature coefficient of viscosity in the system.

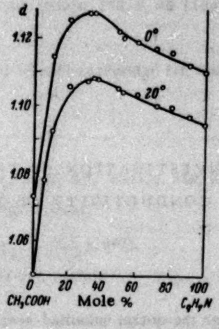

Fig. 2. Density at 0 and 20°.

TABLE 1

Quinoline Content Mole %	Viscosity (in poises)		$\gamma \cdot 10^3$	Density (g/cm³)	
	0°	20°		0°	20°
0.00	—	0.01232	—	1.0732	1.0491
5.44	—	0.0280	—	—	1.0773
10.01	0.0903	0.0509	1.99	1.1139	1.0917
15.09	—	0.0628	—	—	1.1013
19.97	0.1859	0.0761	5.98	1.1254	1.1057
30.55	0.2044	0.0811	6.16	1.1269	1.1067
32.71	0.2073	0.0817	6.28	1.1271	1.1078
35.25	—	0.0804	—	—	1.1068
48.21	0.1630	0.0713	4.58	1.1221	1.1050
51.00	0.1514	0.0690	4.11	1.1199	1.1041
53.00	—	0.0667	—	—	1.1040
59.62	0.1213	0.0609	3.02	1.1191	1.1038
65.46	—	0.0555	—	—	1.1030
69.98	0.0947	0.0526	2.10	1.1171	1.1005
80.08	0.0797	0.0455	1.71	1.1167	1.1001
90.62	0.0696	0.0408	1.44	1.1122	1.0968
100.00	0.0634	0.0376	—	1.1107	1.0939

Viscosity and density. The viscosity of the system was measured at 0° and 20°. Measurements were made with a closed type of viscometer. Results are set forth in Table 1, and the corresponding viscosity isotherms are plotted in Fig. 1. At the bottom of the same diagram is plotted the curve of the temperature coefficient of viscosity, calculated from the formula $\gamma = \frac{\eta_0 - \eta_{20}}{20}$.

The density was measured with a pycnometer. Results are included in Table 1. The density isotherms of the system are plotted in Fig. 2.

Electrical conductivity. Measurements were made with a cell with a ground-glass stopper and unplatinized electrodes. Measurements were performed at a temperature of 20 ± 0.1°, using an improved form of the Kohlrausch bridge, commonly used for measuring the conductivity of non-aqueous solutions.

For preparation of solutions in methyl alcohol we made use of solutions of the binary system quinoline-acetic acid which we had used for measurement of viscosity and density. In special experiments we established that the electrical conductivity of solutions of the binary system did not change with passage of time. In these special experiments we measured the specific electrical conductivity of all the solutions of the system three days after their preparation, and then after 30 days and 80 days. In all these cases the specific electrical conductivity remained constant within the limits of experimental error.

TABLE 2

Preparation No.	Quinoline Content (mole %)	Spec.elec. conductivity $\kappa \cdot 10^5$ ohm^{-1}cm^{-1}			
		2.0 м.	1.0 м.	0.1 м.	0.01 м.
1	0	2.98	1.63	0.82	1.79
2	5.44	—	11.7	—	—
3	10.01	26.5	13.9	2.30	1.97
4	19.97	31.2	17.4	3.02	1.82
5	30.55	32.5	17.7	2.71	1.81
6	35.25	—	19.3	—	—
7	40.00	28.6	—	2.65	1.75
8	51.00	26.5	17.2	2.78	1.87
9	59.62	22.2	14.0	2.53	1.80
10	69.98	18.3	13.1	2.55	1.74
11	80.08	13.4	10.7	2.55	1.66
12	90.62	9.23	6.5	2.16	1.66
13	100.00	0.91	0.42	1.04	1.14

By dissolving weighed amounts of mixtures of the binary system in anhydrous methyl alcohol, we obtained solutions of the ternary system in which the over-all molar concentration of quinoline and acetic acid was constant, while the ratio of these components was varied. In Table 2 are set forth the results of measurements of the specific electrical conductivity of such isoconcentrates. For determination of the dependence of the influence of the over-all concentration of the dissolved substances (quinoline and acetic acid) on the character of the diagram of electrical conductivity of the ternary system, we took various isoconcentrates – 2.0, 1.0, 0.1 and 0.01 M solutions.

In Figs. 3 and 4 are plotted the isotherms of specific electrical conductivity of these solutions.

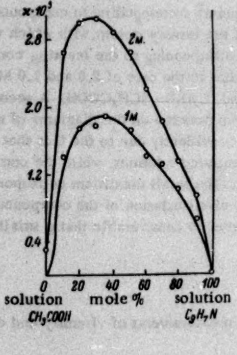

Fig. 3. Electrical conductivity of isoconcentrated solutions of acetic acid and quinoline in methyl alcohol.

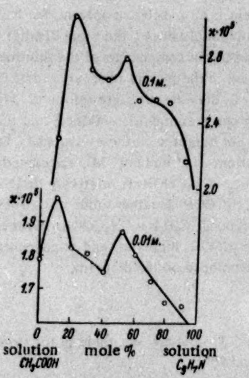

Fig. 4. Electrical conductivity of isoconcentrated solutions of acetic acid and quinoline in methyl alcohol.

Evaluation of Results

Our viscosity and density diagrams have maxima corresponding approximately to the composition of 33 mole % quinoline and 67 mole % acid. With falling temperature, these maxima become sharper on the viscosity curves but are not displaced. This type of well-defined maximum, corresponding to 33 mole % quinoline, is given on the curve of the absolute temperature coefficient of viscosity. All this indicates that a compound of the composition $C_9H_7N \cdot 2CH_3COOH$ is formed in the system quinoline-acetic acid. Measurements of the refractive index of this system [2] likewise point to formation of a compound of the same composition. We can, therefore, assume that two compounds are formed in the system: $C_9H_7N \cdot CH_3COOH$, which is detected on the viscosity diagram, and $C_9H_7N \cdot 2CH_3COOH$, which is detected on the diagrams of viscosity, density and refractive index. It is an interesting fact that both these compounds can be detected on the diagrams of specific electrical conductivity of the solutions of this system in an indifferent solvent (methyl alcohol). We see from Figs. 3 and 4 that the diagrams of specific electrical conductivity of the ternary system with high concentration of dissolved substances (2.0 and 1.0 M) have one maximum corresponding to the compound $C_9H_7N \cdot 2CH_3COOH$, but with progressive lowering of concentration of dissolved substances, a second maximum is developed which corresponds to the compound $C_9H_7N \cdot CH_3COOH$. M. N. Klochko [4] and Hölzl [5] had shown that the maximum on the diagrams of electrical conductivity of the ternary liquid systems, in which one of the components is an indifferent liquid, corresponds to a compound formed between the reacting components. As we see from the diagrams, the first maximum, corresponding to the composition $C_9H_7N \cdot 2CH_3COOH$, is displaced in the direction of the pure acid with decreasing concentration of dissolved substances, whereas the position of the second maximum, corresponding to $C_9H_7N \cdot CH_3COOH$, remains unchanged. This is possibly bound up with the fact that the isotherm of electrical conductivity of the binary system quinoline-acetic acid has a well-defined maximum at the composition of 12 mole % acid.

In order to ascertain the influence of the inherent electrical conductivity of the indifferent solvent upon the character of the electrical conductivity isotherm of the ternary system, we took methyl alcohol which after purification had a different specific electrical conductivity. Thus, all the above-mentioned solutions were made up with alcohol whose inherent specific electrical conductivity was $\kappa_{20} = 52 \cdot 10^{-7}$ ohm^{-1} cm^{-1}.

In addition we made up the same solutions with alcohol whose electrical conductivity after purification was 71.10^{-7} ohm^{-1} cm^{-1}.

In all these cases the isotherms of specific electrical conductivity of the solutions of the ternary system also had two maxima corresponding to the same compositions as on our previous isotherms (Figs. 3 and 4). Only the absolute values of the specific electrical conductivity of the solutions were correspondingly higher.

On the basis of analysis of the diagrams of electrical conductivity of ternary systems in which one component is an indifferent solvent, M. A. Klochko expressed the opinion [4] that the higher the concentration of dissolved substances, the more distinct should be the characteristic points corresponding to compounds formed between the components of the solution. This is because the cuts of the ternary system, with which we are concerned in the present case, are closer to the lateral binary system, corresponding to the reacting components, than in the case of dilute solutions. We see from our Figs. 3 and 4 that in the case of 2.0 and 1.0 M solutions only one maximum is obtained, and this corresponds to the compound $C_9H_7N \cdot 2CH_3COOH$. A second compound was not detected on these diagrams. On the other hand, there are two maxima on the diagrams of more dilute solutions (0.1 and 0.01 M), corresponding to two compounds. This is evidently due to the fact that the compound $C_9H_7N \cdot CH_3COOH$ is relatively little dissociated into ions in concentrated solutions, while the compound $C_9H_7N \cdot 2CH_3COOH$ is rather more strongly ionized and therefore suppresses the small maximum corresponding to the compound $C_9H_7N \cdot CH_3COOH$. With increasing dilution the degree of dissociation of the compound $C_9H_7N \cdot CH_3COOH$ increases, and at concentrations of 0.1-0.01 M it becomes so considerable that a small maximum is developed on the diagram.

SUMMARY

1. A study was made of the system quinoline-acetic acid by measurements of viscosity and density at 0 and 20°.

2. The specific electrical conductivity of solutions of the binary system in an indifferent solvent (methyl alcohol) were measured.

3. Both the diagrams of viscosity and density and the diagrams of electrical conductivity in an indifferent solvent indicate the formation of the compounds $C_9H_7N \cdot CH_3COOH$ and $C_9H_7N \cdot 2CH_3COOH$.

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Received May 7, 1955

Lvov Institute of Medicine

COMPLEX VANADYL COMPOUNDS

II. CITRATE COMPLEXES

V. L. Zolotavin and N. N. Kalugina

Very little attention has been paid in the literature to the problem of vanadyl citrate complexes. Canneri [1] mentions the impossibility of formation by vanadyl ions of complex compounds with citric acid. Ducret [2] demonstrates the existence of two complex ions: a complex containing 1 vanadyl ion per mole citric acid and a complex in which 2 vanadyl ions are bound to 1 mole acid. They are stable in an alkaline medium up to pH 9 (no information is given about their stability in an acid medium). Ducret studied vanadyl citrate complexes only by one method – by neutralization with alkali of a solution containing vanadyl perchlorate and neutral sodium citrate in various ratios and evaluation of the plotted curves. In our opinion, this method does not fully reflect the entire process; moreover, on the basis of the results obtained by only one method, it is difficult to demonstrate the existence of one complex ion or another with sufficient certainty. In an earlier study of the action of sodium citrate on the process of reduction of the vanadyl ion at the dropping mercury cathode, V. L. Zolotavin and T. A. Soboleva [3] had demonstrated the occurrence of complex formation and the very high stability of the complex formed. But in view of the irreversibility of the electrode process in question, which was confirmed by the same authors [4], it was impossible to employ the polarographic method for determination of the composition of this complex.

The purpose of the present investigation was a detailed study of vanadyl citrate complexes. As in the case of the tartrate complexes [11], the investigation was based on physicochemical analysis. Use was made of the method of continuous changes [5,6] and of the method of limited logarithmic plotting [7]. Observations were made of the change of optical density (D), electrical conductivity (w), hydrogen ion concentration (pH), and a correction was introduced for the properties of solutions of the starting substances; composition/property graphs were plotted. A study was made of systems consisting of vanadyl sulfate, citric acid (or its sodium salts) and water. The apparatus described earlier [11] was used.

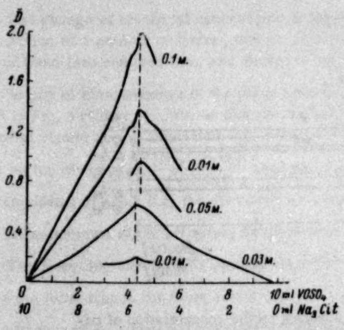

Fig. 1. Course of change of optical density of solutions as functions of the ratios of concentrations of vanadyl sulfate and trisodium citrate with various over-all concentrations of the latter.

I. System $VOSO_4-Na_3C_6H_5O_7-H_2O$

Preliminary study of the spectral characteristics of solutions of vanadyl sulfate and of the citrate complex formed in this system showed that the maximum value of optical density is reached with a yellow light filter – No. 4 (M-57) – and a red light filter – No. 2 (M-66). All later experiments on determination of the optical density were therefore performed with these light filters.

The investigations, undertaken by the method of continuous changes (Fig. 1), convincingly demonstrated the presence of distinct maxima at the ratio

$$\frac{[Na_3C_6H_5O_7]}{[VOSO_4]} = 1.3:1.$$

It must be noted in passing that this position of the maxima is observed when using both light filters. In the opinion of Vosburg [8], this points to the predominance in solution under these conditions of one particular colored complex compound.*

On this basis we may assume the existence in solution of a vanadyl citrate complex compound with the composition $[(VO)_3R_4]^{6-4X}$. (R is here and later the symbol for one of the citric acid anions.)

From the data of Fig. 2, obtained by limited logarithmic plotting, we see that inflection of the curve likewise occurs at a ratio of $\frac{[Na_3C_6H_5O_7]}{[VOSO_4]} = 1.3:1$, which fully confirms the above assumption about the composition of the complex ion.

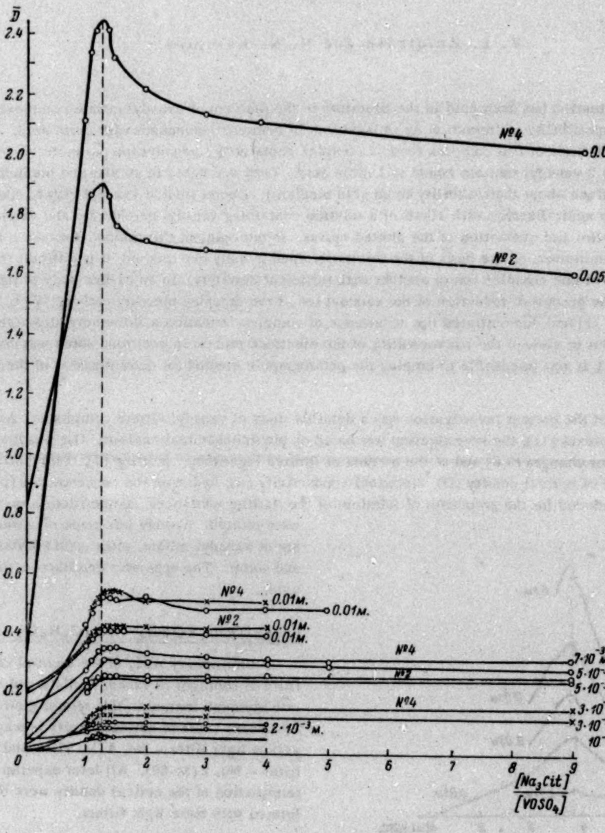

Fig. 2. Change of optical density of solutions in dependence on the concentration of trisodium citrate at various over-all concentrations of the solutions.

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*This observation is also valid for the remaining systems considered in this paper.

On the other hand, on the curves obtained for solutions with a total concentration of $1 \cdot 10^{-2}$–$5 \cdot 10^{-2}$ M, maxima are clearly defined which coincide with the position of the turning points on the remaining curves. These maxima show that when the ratio $\frac{[Na_3C_6H_5O_7]}{[VOSO_4]}$ becomes larger than 1.3:1, a new complex compound starts to form in the solution with another value of the optical density. The fact that in our experiments the position of the maximum of $\overline{D}$ in Fig. 2 coincides in composition with that previously found, is evidence of the low dissociation of the complex ion $[(VO)_3R_4]^{6-4X}$.*

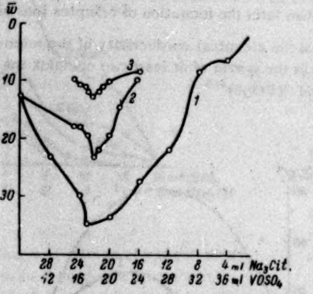

Fig. 3. Change of electrical conductivity of the solutions in dependence upon the value of the ratio of concentrations of vanadyl sulfate and trisodium citrate at various over-all concentrations of the latter.
1) $C = 5 \cdot 10^{-2}$ M, 2) $C = 3 \cdot 10^{-2}$ M, 3) $C = 10^{-2}$ M.

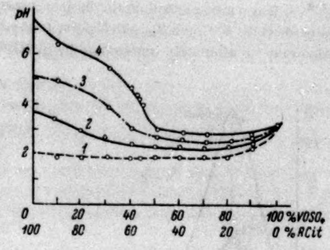

Fig. 4. Change of pH of the solutions in dependence upon the value of the ratio of vanadyl sulfate to citric acid or its salts for an over-all concentration of the solution of 0.05 M.
1) citric acid, 2) monosodium citrate, 3) disodium citrate, 4) trisodium citrate.

In the conductometric investigation, the experiments were carried out only by the method of continuous changes. From Fig. 3 (composition/property plots), we see that the electrical conductivity falls, thus pointing to a process of complex formation; the position of the maxima supports the earlier theory of the composition of the complex formed under these conditions.

The change of electrical conductivity of the solution (a fall in the present case) can be explained as due to the action of a number of factors, such as fall in the total number of ions in solution due to combining of some of them into complex ions, and change in the magnitude of the ionic charge.

Results of measurements of the pH of solutions, obtained by the method of continuous changes, are represented in Fig. 4 (Curve 4). We see that the increase in content of vanadyl ions with simultaneous fall in the number of citrate ions is associated with a marked change in the pH of the solutions which is particularly sharp in the region of ratios of $\frac{[Na_3C_6H_5O_7]}{[VOSO_4]}$ close to 1.33. It must be pointed out in this connection that at a ratio of the components of about 0.5, the pH values are lower than in the original solution of vanadyl sulfate.**

Measurements of the pH values by the method of limited logarithmic plotting revealed a similar process.

The foregoing experiments confirm the existence of a complex ion $[(VO)_3R_4]^{6-4X}$ and permit the assumption of the formation in the more acidic region of a new complex ion at a $\frac{[Na_3C_6H_5O_7]}{[VOSO_4]}$ ratio of 0.5, whose composition may be arbitrarily represented by the formula $[(VO)_2R]^{4-X}$. This ion either does not possess a strong and characteristic color or is only formed in minute amount under these conditions, for which reason it was not detected by the spectrophotometric method; furthermore, the change of electrical conductivity of the solution (associated with formation of the ion) evidently does not exert a specific effect upon the general course of the process.*

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*It should be noted that Ducret [2] plotted his results essentially only by the method of limited logarithmic plotting.

**The original vanadyl sulfate solution had pH 3.3; the sodium citrate solution had pH 7.4.

II. System $VOSO_4-Na_2HC_6H_5O_7-H_2O$

The complex ions formed in this system are likewise colored violet. Measurement of the optical density by the method of continuous changes gave the results which are plotted in Fig. 5. The curves have a strong maximum at a ratio of $\frac{[Na_2HC_6H_5O_7]}{[VOSO_4]} = 2$, on the basis of which we can infer the formation of complex ions of $[(VO)R_2]^{2-2X}$. The curve plotted on the basis of measurement of the electrical conductivity of the solutions has two sharp peaks (Fig. 6, Curve 3), which point to the formation in the system of at least two complex ions whose composition may be arbitrarily represented by $[(VO)R_2]^{2-2X}$ and $[(VO)_2R]^{4-X}$.

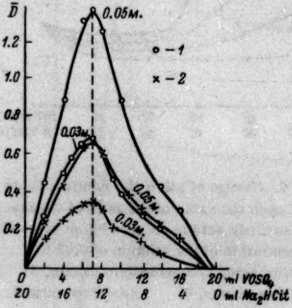

Fig. 5. Course of change of optical density of solutions in dependence upon the ratio of concentrations of vanadyl sulfate and disodium citrate with various over-all concentrations of solutions.
1) Light filter No. 4, 2) light filter No. 2.

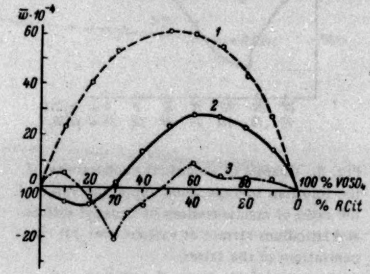

Fig. 6. Course of change of electrical conductivity of solutions in dependence upon the concentrations of vanadyl sulfate and citric acid or its salts with an over-all concentration of the solution of 0.05 M.
1) Citric acid; 2) monosodium citrate;
3) disodium citrate.

Curve 3 in Fig. 4 shows, on the one hand, the sharp drop in pH in the region of $\frac{[Na_2HC_6H_5O_7]}{[VOSO_4]}$ ratios of 1.5 to 4, and, on the other hand, the attainment of minimum pH (2.5) at a ratio of 0.5. The rapid fall in pH may be associated with formation under these conditions of the complex $[(VO)R_2]^{2-2X}$; its fall to 2.5 confirms the above suggestion of the existence of the complex ion $[(VO)_2R]^{4-X}$.

III. System $VOSO_4-NaH_2C_6H_5O_7-H_2O$

Investigation by the spectrophotometric method showed (Fig. 7) that the maximum value of $\overline{D}$ occurs at a ratio of $\frac{[NaH_2C_6H_5O_7]}{[VOSO_4]} = 4$; on this basis we can infer the existence under these conditions of a complex ion in which one vanadyl ion is associated with four citric acid ions: $[(VO)R_4]^{2-4X}$. The $\overline{D}$/composition curve for this system, however, differs appreciably in character from the corresponding curves obtained in the study of the system with di- and trisubstituted citrates. In the region of ratios of $\frac{[NaH_2C_6H_5O_7]}{[VOSO_4]}$ between 8:12 and 16:4 on this curve, there is a very gradual portion which indicates the possibility of existence in this region of one complex ion whose composition could not be determined from Fig. 7.

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*The compositions of the addends will be considered below.

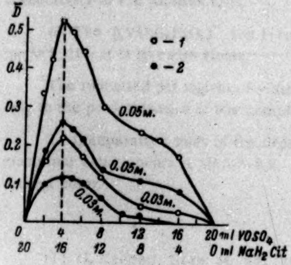

Fig. 7. Course of change of optical density of solutions in dependence upon the ratio of concentrations of vanadyl sulfate and monosodium citrate with various over-all concentrations of the latter.
1) Light filter No. 4, 2) light filter No. 2.

In Fig. 6, Curve 2 (data obtained by the conductometric method), two peaks are clearly visible at ratios of $\frac{[NaH_2C_6H_5O_7]}{[VOSO_4]}$ of 4 and 0.5, respectively. These indicate the existence in this system of at least two complex ions. This observation confirms the data obtained by the spectrophotometric method for the composition of the first of these ions, $[(VO)R_4]^{4-2x}$, and also permits us to assign the formula $[(VO)_2R]^{4-x}$ to the second.

Data obtained by pH measurements (Fig. 4, Curve 2) indicate a considerable fall in pH with decreasing ratio of $\frac{[NaH_2C_6H_5O_7]}{[VOSO_4]}$. At the point corresponding to the ratio of 0.5, the pH is a minimum and considerably lower than in the original solution of vanadyl sulfate; in the light of the earlier observations, this is associated with formation of the complex ion $[(VO)_2R]^{4-x}$.

IV. System $VOSO_4$–$H_3C_6H_5O_7$–H_2O

Interaction of vanadyl sulfate with citric acid does not give a color change of the solution detectable by the eye. A study of the system by all three methods did not bring to light any specific data that would permit us to formulate the composition of the complexes; the changes observed in the values of $\overline{D}$, $\overline{w}$, and pH only indicate the occurrence of complex formation (Curve 1 in Fig. 4 and Curve 1 in Fig. 6).

V. Influence of Rise of pH on the Composition of the Complex Ion $[(VO)_3R_4]^{6-4x}$

The system $VOSO_4$–$Na_3C_6H_5O_7$–H_2O was investigated by the spectrophotometric method, similarly to the above, but with the difference that preliminary addition was made to the sodium citrate solution of steadily increasing amounts of alkali while keeping the total volume and concentration of the solution of the complex compound unchanged.

The data of Fig. 8 show that the first rise in pH is accompanied by displacement of the maximum of the optical density; starting from pH 4.5, this maximum corresponds invariably to the ratio $\frac{[Na_3C_6H_5O_7]}{[VOSO_4]} = 1$. On this basis we may assume the existence of yet another complex ion with the composition $[(VO)R]^{2-x}$, formed in a weakly acid medium and stable at relatively high values of pH of solutions.

VI. The Composition of the Addends

For the elucidation of the composition of the addends we must consider the dependence of the dissociation of citric acid on the pH. On the basis of the literature data [9,10], we can assume that in the complex ion $[(VO)_2R]^{4-x}$, which predominates at a pH of about 2.5, the addend is the ion of $H_2C_6H_5O_7^-$, the percentage content of which in this pH region is 10-26% of the total content of citric acid and of all its anions. With such a relatively low content of ions of $H_2C_6H_5O_7^-$, the concentration of the derived complex ions of $[(VO)_2H_2C_6H_5O_7]^{3+}$ must likewise be low; we thus account for the fact that the formation of these ions cannot be detected spectrophotometrically.

On the basis of the predominating content of $H_2C_6H_5O_7^-$ ions at pH 3-4, amounting to 52-67%, we may assume that they actually also enter into the composition of the other three complex ions whose compositions are now represented thus: $[(VO)(H_2C_6H_5O_7)_4]^{2-}$, $[(VO)(H_2C_6H_5O_7)_2]^0$ and $[(VO)_3(H_2C_6H_5O_7)_4]^{2+}$.

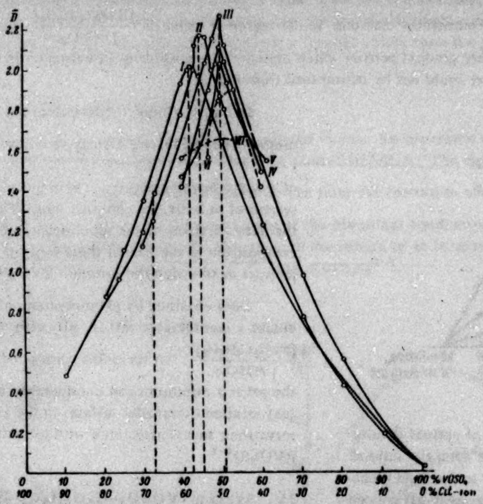

Fig. 8. Change of composition of the complex $[(VO)_3R_4]^{6-4X}$ with changing pH.
I) pH 3.7, II) pH 4.0, III) pH 4.5, IV) pH 4.9, V) pH 7.1, VI) pH 9.1, VII) pH 9.5.

The addend can be the anion of $C_6H_5O_7^{3-}$ only in the last of the above-described complexes which exists at relatively high pH values; under these conditions the anion in question predominates; the composition of this compound can then be represented by the formula $[(VO)C_6H_5O_7]^-$.

The fuller information obtained for the composition of the complexes enables us to consider the problem of the cause of the fall of pH and of the rise of electrical conductivity observed in the formation of the $[(VO)_2H_2C_6H_5O_7]^{3+}$ ion. The explanation is that the sulfuric acid formed during hydrolysis leads to the appearance of sodium bisulfate in solution. This is shown by the over-all equation:

$$4VOSO_4 + 2Na_3C_6H_5O_7 + 6H_2O = 2[(VO)_2H_2C_6H_5O_7](OH)_3 + 2NaHSO_4 + 2Na_2SO_4.$$

The presence of free hydrogen ions naturally leads to fall in pH and to rise in electrical conductivity.

SUMMARY

1. It was established that reaction of vanadyl sulfate with citric acid and its salts gives several complexes.

2. It was shown that the composition of the complexes is governed by the magnitude of the pH.

a) The $[(VO)_2H_2C_6H_5O_7]^{3+}$ ion is formed at a pH of about 2.5 and is detected in all three systems. It is suggested that the concentration of this ion is low, due to which it was not found by the spectrophotometric method. (For the same reason the question of its color remains open.) Its formation is bound up with falling pH and increasing electrical conductivity.

b) The violet $[(VO)(H_2C_6H_5O_7)_4]^{2-}$ ion is formed at pH 2.6-3.0. Its formation is accompanied by a fall in electrical conductivity of the solution.

c) In the pH region 3.0-3.5 the compound $[(VO)(H_2C_6H_5O_7)_2]$ exists; it is also violet; its presence in solution is bound up with falling electrical conductivity.

d) The violet-colored $[(VO)_3(H_2C_6H_5O_7)_4]^{2+}$ ion is formed at pH 3.5-4.5; in its presence the electrical conductivity of the solution falls.

e) The $[(VO)C_6H_5O_7]^-$ ion is formed in a weakly acid medium and is stable at relatively high pH values (up to 9-10); it is likewise violet.

The indicated pH regions of existence of each complex are arbitrary; they should be understood to relate only to the predominance of one complex in relation to others existing at very similar pH values.

3. Comparative study of the dependence of the optical density of the solution on the pH showed that its maximum value occurs at pH 3.8-3.9. We can therefore conclude that the $[(VO)_3(H_2C_6H_5O_7)_4]^{2+}$ ion has the deepest color.

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Received June 17, 1955

S. M. Kirov Ural Polytechnic Institute

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*T.p. = C. B. Translation pagination.

COMPLEX COMPOUNDS OF PHOSPHORUS PENTACHLORIDE WITH CHLORIDES OF SOME ELEMENTS

IV. THE SYSTEM PHOSPHORUS PENTACHLORIDE-TIN CHLORIDE

Ya. B. Buryanov

In the preceding communications [1,2] results were presented of an investigation of the process of complex formation in systems consisting of phosphorus pentachloride and chlorides of aluminum and iron, and also of the complex compounds formed in these systems. The investigations showed that phosphorus pentachloride enters into the composition of the $[PCl_4]^+$ ion in these compounds.

It appeared of interest to continue this work in the direction of study of the system PCl_5-SnCl_4, particularly since the literature contains conflicting data for the composition of the compound of these two chlorides.

Casselmann [3] heated a mixture of phosphorus trichloride with the complex $SnCl_4 \cdot 2SCl_4$ in a stream of dry hydrogen chloride and obtained a product in the form of lustrous, colorless crystals to which he assigned the formula $SnCl_4 \cdot PCl_5$, formed by the reaction:

$$SnCl_4 \cdot 2SCl_4 + 3PCl_3 = SnCl_4 \cdot PCl_5 + 2PCl_5 + S_2Cl_2.$$

According to Casselmann the compound $PCl_5 \cdot SnCl_4$ can also be obtained by direct interaction of both chlorides by heating. Only tin chloride distills over at 120-130°; at 140-160° pure phosphorus pentachloride comes over; the compound $PCl_5 \cdot SnCl_4$ remains behind and sublimes at 200-220°.

Baudrimont [4] obtained a compound of phosphorus pentachloride with tin chloride by the action of excess PCl_5 on metallic tin:

$$3PCl_5 + Sn = 2PCl_3 + PCl_5 \cdot SnCl_4.$$

According to this author, the compound forms lustrous, nacreous white needles, volatilizing at 220° with decomposition. Water decomposes it, giving a gelatinous mass containing the whole of the phosphorus and tin.

Although Casselmann and Baudrimont assign the formula $PCl_5 \cdot SnCl_4$ to their compound of phosphorus pentachloride with tin chloride, the formula $2PCl_5 \cdot SnCl_4$ is sometimes given for this compound in the literature, for example, in Abegg's Handbook [5], which also cites the above-mentioned authors.

We carried out a study of solutions of the system PCl_5-SnCl_4 in non-aqueous solvents by several methods of physicochemical analysis.

EXPERIMENTAL

Tin chloride was prepared by chlorination of fused metallic tin [6]. The product was kept for about an hour with a small quantity of tin foil for removal of dissolved chlorine and then distilled. The fraction boiling at 114.3° was collected. The product was stored in sealed ampoules.

Preparation and storage of the remaining preparations have been described before [1,2].

We were unable to carry out a thermal analysis of the system PCl_5-SnCl_4. Addition of phosphorus pentachloride to tin chloride results at once in formation of a white precipitate which could not be fused due to its ease of sublimation. On further addition of phosphorus pentachloride, the amount of crystalline substance formed increases but the amount of liquid phase ($SnCl_4$) steadily decreases. Only on reaching a molar ratio of PCl_5 to $SnCl_4$ equal to 2 does the liquid phase completely disappear and the substance formed appears to be dry. When larger amounts of PCl_5 are added, no reaction is observed on heating, and the system consisted of two solid phases: a white product and unchanged PCl_5.

Consequently, a study of the fusibility of the system PCl_5-SnCl_4 only gave indirect evidence of the formation of the compound $2PCl_5 \cdot SnCl_4$.

Investigation of Solutions of the System PCl_5-SnCl_4 in Non-aqueous Solvents

The specific electrical conductivity of this system was measured in nitrobenzene and acetonitrile with constant molar ratio of one of the components to solvent; it was also measured at constant over-all molar concentration of both chlorides. Measurements were performed at 25 and 45° (± 0.05). The procedure has been described before [2].

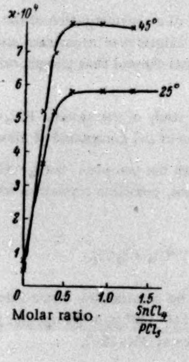

Fig. 1. Specific electrical conductivity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ at a $PCl_5/C_6H_5NO_2$ ratio of 1:195.6.

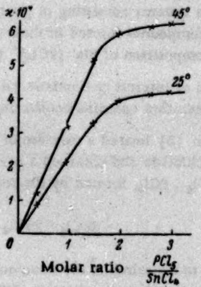

Fig. 2. Specific electrical conductivity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ at a $SnCl_4/C_6H_5NO_2$ ratio of 1:557.

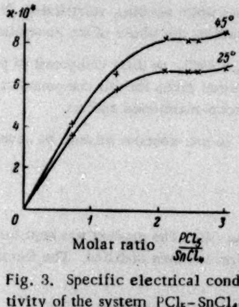

Fig. 3. Specific electrical conductivity of the system $PCl_5-SnCl_4-CH_3CN$ at $SnCl_4/CH_3CN$ molar ratio of 1:203.4.

In Fig. 1 are plotted the results of measurements of the electrical conductivity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ at constant molar ratio of PCl_5 to nitrobenzene (1:195.6), while Figs. 2 and 3 represent the results of measurements of the electrical conductivity of the system PCl_5-SnCl_4–solvent at constant molar ratio of $SnCl_4$ to nitrobenzene (1:557) or to acetonitrile ($SnCl_4:CH_3CN$ = = 1:203.4).

These diagrams show that the specific electrical conductivity of the system PCl_5-SnCl_4–solvent rises with increasing concentration of PCl_5, reaching at 25° and a $PCl_5/SnCl_4$ molar ratio ≃ 2 a value of the order of $4.0 \cdot 10^{-4}$ $ohm^{-1}cm^{-1}$ for nitrobenzene solutions and $6.7 \cdot 10^{-3}$ $ohm^{-1}cm^{-1}$ for acetonitrile solutions.

A sharp inflection is observed on the isotherms of specific electrical conductivity on attainment of a PCl_5/ /$SnCl_4$ molar ratio of 2. Further rise of the PCl_5 concentration has relatively little influence upon the electrical conductivity of the systems.

The specific electrical conductivity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ at constant PCl_5/nitrobenzene molar ratio (Fig. 1) increases with increasing concentration of $SnCl_4$. After attainment of a $SnCl_4/PCl_5$ molar ratio of 0.5, further addition of the non-conducting $SnCl_4$ scarcely alters the electrical conductivity of the system.

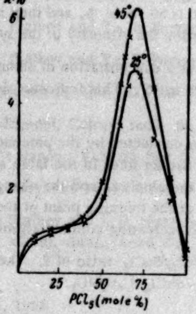

Fig. 4. Specific electrical conductivity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ ($C_{PCl_5} + C_{SnCl_4}$ = 0.035 mole/liter).

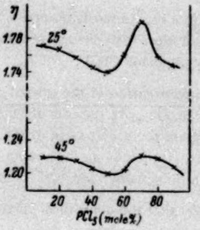

Fig. 5. Viscosity of the system $PCl_5-SnCl_4-C_6H_5NO_2$($C_{PCl_5} + C_{SnCl_4}$ = 0.07 mole/liter).

Crysocopy of the System $PCl_5-SnCl_4-C_6H_5NO_2$ ($C_6H_5NO_2$--8.4665 g, $SnCl_4$-0.0627 g; Δt_0 = 0.02°)

Weight of PCl_5 (in g)	$PCl_5/SnCl_4$ molar ratio	Δt_1	Δt
0.0389	0.79	0.26	0.24
0.0660	1.34	0.39	0.37
0.0932	1.90	0.53	0.51
0.1474	2.99	0.59	0.57
0.1774	3.60	0.62	0.60

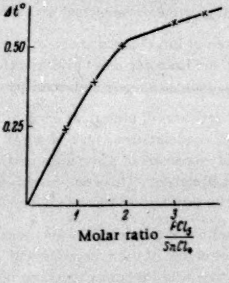

Fig. 6. Cryoscopy of the system PCl_5-SnCl_4--$C_6H_5NO_2$ at $SnCl_4/C_6H_5NO_2$ molar ratio of 1:286.

The rise in electrical conductivity of a nitrobenzene solution of PCl_5 when the non-conducting $SnCl_4$ is added is due to the formation of complex molecules which conduct current.

The specific electrical conductivity of the system $PCl_5-SnCl_4-C_6H_5NO_2$, when measured at constant overall molar concentration of phosphorus pentrachloride and tin chloride (Fig. 4), has a sharp maximum at a PCl_5/ /$SnCl_4$ molar ratio of 2.

The results of these investigations, like the results of measurement of the electrical conductivity at constant molar ratio of PCl_5 or $SnCl_4$ to solvent, lead to the conclusion that these chlorides add on to one another in the solvents with formation of the complex $2PCl_5 \cdot SnCl_4$.

Viscosity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ was measured in a viscometer adapted for work with substances which decompose under the action of atmospheric moisture [7].

The over-all molar concentration of PCl_5 and $SnCl_4$ in the nitrobenzene was 0.07 mole/liter. For calculation of the viscosity we determined the specific gravity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ at 25 and 45°. The specific gravity of this system changes linearly from 1.200 to 1.205 at 25°, and from 1.180 to 1.186 at 45°.

The viscosity was measured at 25 and 45° after holding the viscometer in a thermostat at the measuring temperature (± 0.05) for 15 to 20 minutes. Water was taken as the standard liquid. As Fig. 5 shows, the viscosity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ at both temperatures, with rising concentration of PCl_5, at first falls until the PCl_5 concentration (in relation to the sum of both chlorides) is 50 mole %, and then rises until the concentration is 70 mole % PCl_5. With further rise of PCl_5 concentration the viscosity of the system falls.

Consequently, a maximum is observed on the viscosity isotherms at a concentration of about 70 mole % PCl_5 which does not alter with change of temperature in the range of 25 to 45°. This indicates the presence in the system of the compound $2PCl_5 \cdot SnCl_4$.

Cryoscopic investigation of the system $PCl_5-SnCl_4-C_6H_5NO_2$ was conducted by the procedure of Ya. A. Fialkov and I. D. Muzyka [8]. Results of the cryoscopic measurements are set forth in the table and plotted in Fig. 6. In the diagram the molar ratio of PCl_5 to $SnCl_4$ is plotted on the abscissas and the change of depression $\Delta t = \Delta t_1 - \Delta t_0$ is plotted on the ordinates. Δt_0 is the depression of the freezing point of the original solution of $SnCl_4$ in nitrobenzene, and Δt_1 is the depression observed with increasing concentrations of PCl_5.

The data show that the depression curve changes direction at a $PCl_5/SnCl_4$ ratio of 2. The results confirm the formation of the compound $2PCl_5 \cdot SnCl_4$ in the system $PCl_5-SnCl_4-C_6H_5NO_2$.

Evaluation of Results

The study of the electrical conductivity of the system PCl_5-SnCl_4 in nitrobenzene and acetonitrile has shown (discontinuities on the isotherms of specific electrical conductivity in experiments with constant molar ratio of one or the other component to the solvent, or a sharp maximum on the isotherms of specific electrical conductivity in measurements by the method of isomolar concentrations) formation in the system of an electrically conducting complex compound with a phosphorus pentachloride/tin chloride molar ratio of 2.

Formation of this compound results in a sharp maximum on the curve of specific electrical conductivity of solutions of the isomolar series even in dilute solution – at a concentration of the complex of approximately 0.012 M. This indicates fairly high stability of the complex $2PCl_5 \cdot SnCl_4$ formed in organic solvents.

On the isotherms of electrical conductivity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ (Fig. 4) an inflection is observed in the concentration range of 40-50 mole % PCl_5. This indicates the possible formation in this system also of another compound of phosphorus pentachloride with tin chloride, possibly $PCl_5 \cdot SnCl_4$, mention of which appears in the literature. This compound is probably much less stable than the complex $2PCl_5 \cdot SnCl_4$ and changes into the latter on addition of phosphorus pentachloride.

The results of cryoscopic measurements and of a study of the viscosity of the system $PCl_5-SnCl_4-C_6H_5NO_2$ confirm the formation of the compound with the composition $2PCl_5 \cdot SnCl_4$. Furthermore, a minimum is observed on the viscosity isotherms which corresponds to an equimolar ratio of PCl_5 to $SnCl_4$ and which possibly reflects the formation of another compound of these chlorides as mentioned above.

The molecular weight of the complex $2PCl_5 \cdot SnCl_4$ formed in the system was calculated from the results of cryoscopic measurements (table and Fig. 6). It was found to be 260.2 at a concentration of 1.89 weight %, i.e. about half of the theoretical value (677). This may be due to electrolytic dissociation of the molecules of the complex into three ions.

Comparison of the physicochemical properties of the system PCl_5-SnCl_4 with those of the previously studied systems PCl_5-AlCl_3 and PCl_5-FeCl_3 in organic solvents justifies the assumption that the complex $2PCl_5 \cdot SnCl_4$ has the structure $[PCl_4]_2[SnCl_6]$ and dissociates into ions according to the scheme:

$$[PCl_4]_2[SnCl_6] \rightleftharpoons 2PCl_4^+ + SnCl_6^{--}.$$

In conclusion we wish to convey our sincere thanks to Ya. A. Fialkov for guidance in the research.

SUMMARY

A study was made of the electrical conductivity of the system PCl_5-SnCl_4 in acetonitrile and nitrobenzene and of the viscosimetry and cryoscopy of the same system in nitrobenzene. The formation of an electrically conducting complex $2PCl_5 \cdot SnCl_4$ was demonstrated.

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Received June 14, 1955

Institute of General and Inorganic Chemistry
of the Academy of Sciences of the Ukrainian SSR

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OXIDES OF TRANSITION METALS AS CATALYSTS OF THE OXIDATION OF HYDROCARBONS

L. Ya. Margolis, S. Z. Roginsky and T. A. Gracheva

Oxidative treatment of hydrocarbons long ago attracted the attention of chemists as one of the main directions of heavy organic synthesis. Oxygen combines with hydrocarbons in diverse reactions of addition, substitution and destructive and condensative oxidation [1,2].

Due to the diverse types of oxidative reactions of hydrocarbons, the relative characterization of the catalysts is an extremely difficult task. In the present investigation an attempt is made at such a characterization with the help of the following four reactions of olefins (C_2H_4 and C_3H_6).

1. Drastic oxidation to carbon dioxide and water:

$$C_3H_6 + 4\frac{1}{2}\,O_2 \rightarrow 3CO_2 + H_2O,$$

$$C_2H_4 + 3O_2 \rightarrow 3CO_2 + 2H_2O.$$

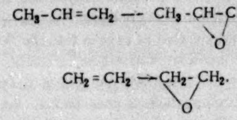
2. Destructive oxidation:

$$CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}CHO + HCHO,$$
$$CH_2{=}CH_2 \rightarrow 2HCHO.$$

3. Selective oxidation of part of the hydrogen, leaving the C–C bonds intact, with formation of acrolein:

$$CH_2{=}CH{-}CH_3 \rightarrow CH_2{=}CH{-}CHO + H_2O.$$

4. Addition of oxygen with formation of propylene oxide or ethylene oxide:



$$CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}\underset{\diagdown\,O\,\diagup}{CH{-}CH_2}$$

$$CH_2{=}CH_2 \rightarrow \underset{\diagdown\,O\,\diagup}{CH_2{-}CH_2}.$$

Oxidation was studied over a series of oxides of transition metals which may be regarded as representatives of oxide catalysts with different types of predominating action.

The course of the individual reactions was followed from the composition of the reaction products. Olefin oxides, aldehydes, acids, CO and CO_2 were determined. Oxidation was carried out under dynamic conditions with mixtures of ethylene or propylene with oxygen in 1:1 ratio, diluted with nitrogen, in the temperature range of 200 to 400°.

The sum of the aldehydes was determined by the hydroxylamine method, and their individual chemical composition by polarography. The acids were titrated with 0.01 N KOH in presence of phenolphthalein. Carbon monoxide and dioxide were determined with the VTI gas analyzer.

Since the activity and selectivity of the catalysts, as also the energy of activation and the kinetic equations of the partial processes, are generally different, the quantitative comparison of the catalysts with differing predominating types of activity requires systematic investigations. The difference in composition of products, even when persisting with wide variations of test conditions, can only qualitatively characterize the specificity of action of the various oxides.

In the table are set forth data for seven simple oxides and two mixed systems which we consider typical. Results obtained at 400° are shown in all cases.

Oxidation of Propylene Over Various Catalysts (carrier – asbestos)

Number	Catalyst	Percent catalyst on carrier	Composition of reaction mixture (in vol.-%)			Composition of products of reaction (in % of reacted hydrocarbon)				
			C_3H_6	O_2	N_2	aldehyde	acrolein	acid	CO	CO_2
	Catalysts of far-reaching oxidation									
1	MnO_2 . . .	30	5	5	90	traces	—	—	0	100
2	NiO	30	5	5	90	traces	—	—	0	100
3	$MgCr_2O_4$ . .	30	10	10	80	traces	0	5	0	94
4	$CuCr_2O_4$ . .	30	10	10	80	traces	0	3	0	97
	Catalysts of destructive oxidation									
5	V_2O_{5-x} . .	10	10	10	80	15*	traces	27	37	20
6	M_oO_{3-x} . .	25	10	10	80	8	—	21	39	27
7	WO_{3-x} . .	50	10	10	80	2	—	17	54	27
8	UO_{3-x} . . .	30	10	10	80	2	—	10	20	67
	Catalyst of selective oxidation to acrolein									
9	Cu_2O . . .	15	30	10	60	traces	60	0	5	35

The data of the table show that with similar composition of the starting mixture and the same temperature over NiO and MnO_2, substantially the whole of the propylene is oxidized to CO_2 and H_2O without formation of appreciable amounts of intermediate products, i.e. under these conditions Reaction 1 heavily predominates. With lowering of temperature and change of composition, it was still not possible to obtain detectable concentrations of products of mild oxidation. The typical effect of oxides of metals of the 6th group of the Periodic System (MoO_3, WO_3, and UO_3) as well as of oxides of the 5th group (V_2O_5)** was found to be mild oxidation with rupture of the carbon skeleton and formation of formaldehyde and acetaldehyde, as well as formic and acetic acids. The extent of drastic oxidation depends upon the conditions of the process. Cuprous oxide behaves unusually; over this catalyst, the introduction of oxygen into the molecule can take place without rupture of the double bond with formation of the unsaturated aldehyde, acrolein. Thus, on passing through Cu_2O a mixture of propylene, oxygen, nitrogen and steam (25:5:9:61) at 350-400° (duration of contact 2 seconds) the ratio of acrolein to carbon dioxide in the reaction products is close to 2:1. Formaldehyde was not detected at all and only traces of acetaldehyde were found. Change of composition of the starting mixture, of the temperature and of the duration of contact only led to changes in the carbon dioxide/acrolein ratio in the products of oxidation. In this connection attention may be drawn to foreign patents [1] on the production of acrolein over cuprous oxide and various copper salts with good selectivity. The possibility of oxidation of an unsaturated hydrocarbon without rupture of the double bond is of great theoretical interest. As we know, some oxidizing agents ($KMnO_4$, etc.)

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*Acetaldehyde 5% + formaldehyde 10%.

**During reaction the oxides of the metals (V_2O_5, MoO_3 and WO_3) are partially reduced with formation of V_2O_4, MoO_2, etc. During reaction, the catalysts are a mixture of penta- and tetravalent oxides of the metals.

cause oxygen to add on at the double bond. Asymmetry of the double bond (σ-π conjugation) leads to change of reactivity of the hydrogen atoms attached to carbon in the 2-position relative to the double bond [3]. Over cuprous oxide the attack of oxygen is not directed at the double bond, as for example, in the case of oxidation of ethylene to ethylene oxide, but is directed at the methyl group.

Similar data were obtained in the isotopic exchange of hydrogen [4,5]; the same workers demonstrate the particular mobility of this atom of hydrogen. The character of the drastic oxidation proceeding at the same time as formation of acrolein is not yet clear. In this case also, it is probable that mainly parallel independent oxidation of the olefin and not of the acrolein will take place, but this hypothesis requires to be checked with the help of C^{14}-labeled molecules.

In conclusion, let us briefly consider this problem from the electronic aspect. The activity of catalysts in oxidation reactions is assumed to be associated with the presence of unfilled d-shells, which is most simply explained by the formation of d—s-bonds [6]. It is therefore possible that catalysts of drastic oxidation (oxides of U, W, Mn, Ni, etc.) do not fortuitously contain a large number of empty sites in the d-shells.

Silver does not contain free d-electrons; we believe, however, that during oxidative catalysis the silver is modified by oxygen which removes some of its d-electrons, thus making it more similar to palladium. In other words, a certain number of atoms with gaps in the d-shell are present in the silver lattice which consists of atoms with completely filled d-shells. Unoccupied d-levels are developed in the lattice of the metal.* Nor, probably, is it fortuitous that the mildest oxidation is observed over silver – direct addition of oxygen with rupture of the π-bond in the olefin. In the cuprous oxide lattice (similarly to metallic silver) the normal metallic ions do not have gaps in the d-shell, but these gaps appear on transition to Cu^{++} in Cu_2O which always contains some cupric oxide. The number of such centers in Cu_2O is considerably greater than the number of Ag^{++} or Ag^{+++} in silver, and over Cu_2O oxygen adds on to the olefin molecule. Thus a certain parallelism is observed between completion of the d-zone of the catalyst and the direction of the oxidation process which merits further investigation.

SUMMARY

1. A study was made of the oxidation of propylene over typical oxidation catalysts (simple oxides of metals and binary chromites).

2. The specificity of action of different oxides of metals and the possibility of oxidation of an unsaturated hydrocarbon without rupture of the double bond were demonstrated.

3. A relation is observed between completion of the d-zone of catalyst and the direction of the oxidation process.

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Received June 7, 1955

Institute of Physical Chemistry
Academy of Sciences of the USSR

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*In part they can also be formed without oxygen, due to thermal movement.

**T.p. = C. B. Translation pagination.

PHYSICOCHEMICAL INVESTIGATION OF DIOXANE-CONTAINING SYSTEMS

X. SOME PHYSICOCHEMICAL PROPERTIES OF DIOXANE SOLUTIONS OF PYROSULFURIC ACID*

Ya. F. Mezhenny

The properties of dioxane solutions of hydrogen chloride [1,2] and sulfuric acid [3] were previously described. The fusibility diagram of the system dioxane-pyrosulfuric acid has also been studied [4]. In the present investigation some other properties of this system were studied, namely the electrical conductivity, the thermal effect of interaction, and the decomposition potential. The starting substances were prepared and stored as described earlier [4].

1. Thermal effect of interaction of pyrosulfuric acid with dioxane. This reaction, leading to formation of the compound $H_2S_2O_7 \cdot 2C_4H_8O_2$, is accompanied by considerable evolution of heat. An adiabatic calorimetric apparatus [5] was used for measurement of the thermal effect of this interaction. Adiabatic conditions were realized by adding cold or hot water to the jacket of the calorimeter. The water equivalent of the calorimeter was 191.87; it was determined by the method of Joule and Lents using a silver coulometer [6]. In three experiments with samples weighing 1-3 grams, the values of the thermal effect were found to be 42.35, 41.93 and 42.13 kcal/mole. The mean value is Q = 42.137 kcal/mole.

TABLE 1

Specific Electrical Conductivity of Pyrosulfuric Acid in Dependence on the Temperature

$t°$	50	48	47	45	44	43	42	41	40	38	36	35**
$\varkappa \cdot 10^3$	11.25	11.05	10.82	10.06	10.0	9.82	9.34	8.87	8.40	7.46	7.32	6.86

As we see, the thermal effect of formation of an acido-oxonium compound – the dioxanate of pyrosulfuric acid – is twice as high as the effect of the reaction of formation of sulfuric acid from water and sulfur trioxide.

We know that complex compounds include those "... formed by sequestration of components not associated with the development of new electron pairs" [7]. And although in them "... interaction occurs between the components which is not predicted by the classical doctrine of valence" [8], the thermal effects of their formation are of the same order as for ordinary compounds.

2. Results of measurements of electrical conductivity. At the start the electrical conductivity of pyrosulfuric acid was measured. The conductivity of dioxane is known from the literature [9].

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*Submitted to the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Ukrainian SSR.

**On further cooling, the liquid started to crystallize.

Subsequently, addition* was made to the pyrosulfuric acid of puredioxane which had been stored in sealed test tubes, and the specific electrical conductivity was measured in dependence on the temperature.

The plotted results (Fig. 1) show that with 5.18 mole % dioxane the curve of specific electrical conductivity is situated higher than for the system containing 25.11 mole % (Curve II) dioxane. The curve for the system containing 55.01% (Curve III) is considerably lower and more gradual. The specific electrical conductivity of the system with 69.49 mole % (Curve IV) is situated still lower and it changes relatively little with rise of temperature. In another series of experiments in the range of 32-96.8 mole % dioxane the values of specific electrical conductivity of the system pyrosulfuric acid-dioxane set forth in Table 2 were obtained.

The specific electrical conductivities of the system dioxane-pyrosulfuric acid in dependence on change of composition at constant temperature (50 and 40°) are compared in Table 3.

The composition/ specific electrical conductivity diagram (Fig. 2), plotted from the data of Table 3, shows that at 50° the Curve I has a maximum on the pyrosulfuric acid side. The same maximum, but not so sharp, is also observed (Curve II) at 40°. The diagram represents one of the cases in a paper by M. A. Klockho [10].

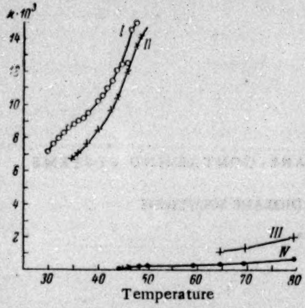

Fig. 1. Influence of temperature upon the specific electrical conductivity of dioxane solutions of pyrosulfuric acid.
I) 5.18 mole % dioxane, II) 25.11 mole % dioxane, III) 55.01 mole % dioxane, IV) 69.49 mole % dioxane.

TABLE 2

Specific Electrical Conductivity of the System Dioxane-Pyrosulfuric Acid in Dependence on Composition and Temperature

Content of dioxane (mole%)	Temperature	$\varkappa \cdot 10^3$
32.15	70°	13.35
50.03	70	6.55
67.50	77	0.994
72.99	85	0.229
76.42	74	0.168
89.6	70	0.154
	26.0	0.0294
	28.0	0.0320
	30.1	0.0328
	34.0	0.0337
	43.0	0.03461
91.8	20.3	0.04423
93.8	20.3	0.00129
95.01	20.3	0.0005
95.6	20.3	0.000025
96.6	20.3	0.000068

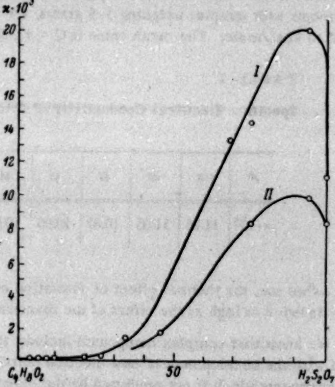

Fig. 2. Composition versus specific electrical conductivity.
I) At 50°, II) at 40°.

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*Due to the very high thermal effect of the reaction, the addition of dioxane in all cases was effected in small portions with intense external cooling.

TABLE 3

Specific Electrical Conductivity of the System Dioxane-Pyrosulfuric Acid in Dependence on the Composition

Content of dioxane (mole %)	0.000	5.18	25.11	55.01*	69.49**	73.99	79.51	85.02	91.9
$\varkappa_{80} \cdot 10^3$	11.25	20.01	14.35	1.099	0.084	0.107	0.068	0.0595	0.0545
$\varkappa_{40} \cdot 10^3$	8.40	9.9	8.34	—	0.0282 ***	0.068	0.051	0.0167	—

TABLE 4

Molecular Electrical Conductivity of Pyrosulfuric Acid in Dioxane

$V \frac{\text{liters}}{\text{mole}}$	0.099	0.194	0.298	0.352	0.500	0.750	0.855	1.17	1.492
$\mu = 1000\varkappa \cdot V$	1.478	0.084	0.1337	0.0876	0.0561	0.022	0.00361	0.00151	0.000734

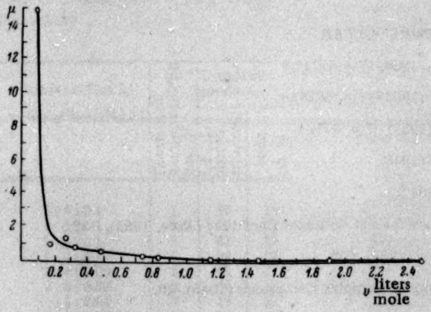

Fig. 3. Dependence of the molecular electrical conductivity of pyrosulfuric acid in dioxane on the dilution.

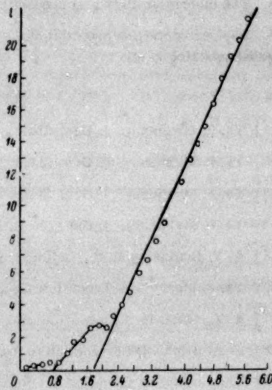

Fig. 4. i/V curve of dioxane solutions of pyrosulfuric acid.

A study was also made of the constancy of the electrical conductivity of the system dioxane-pyrosulfuric acid with time. For this purpose, a solution containing 69.49 mole % dioxane was left in an electrical conductivity cell (well-protected against access of moisture) for 72 hours. Measurement revealed complete constancy of the system during this period.

Values of the molecular electrical conductivity of dioxane solutions of pyrosulfuric acid in dependence on dilution are set forth in Table 4. As we see from these data (and also from Fig. 3) the molecular electrical conductivity of this system adds another to the number of so-called "anomalous" curves discovered by I. A. Kablukov.

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*At 65°.

**At 52°.

***At 44°.

3. The decomposition potential was measured by the method of polarization curves. Results of measurements are plotted in Fig. 4, from which we see that the first marked rise of current strength starts at a potential of 0.84 V. The second prominent decomposition potential was found to be 1.72 V. As we know, approximately the same decomposition potential was obtained for oxygen-containing acids in aqueous solutions.

Evaluation of Results

On the basis of the above data we can assume that the maximum of specific electrical conductivity obtained in Fig. 2 relates to solutions of the complex compound $H_2S_2O_7 \cdot 2C_4H_8O_2$ in pyrosulfuric acid. In this case, we evidently have two electrolytes – pyrosulfuric acid and its complex compound with dioxane. But the solution of pyrosulfuric acid in its complex with dioxane conducts current much more poorly. Even the complex compound is a fairly poor conductor of electricity.

The dilute solutions of the complex compound in dioxane are still poorer conductors of electricity.

SUMMARY

1. The thermal effect of the reaction of formation of the dioxanate of pyrosulfuric acid is equal to 421,137 kcal/mole (in the adiabatic calorimeter).

2. The specific electrical conductivity of the system dioxane-pyrosulfuric acid was investigated with various ratios of components. It was shown that the maximum of the specific electrical conductivity lies in the region of 95 mole % pyrosulfuric acid and has a value of the order of 0.02 at 50°.

3. Rise of temperature increases the specific electrical conductivity of the system dioxane-pyrosulfuric acid.

4. The molecular electrical conductivity of the system has an anomalous character.

5. The decomposition potential of the system is 1.72 V, which is close to the value for aqueous solutions of oxygen-containing acids.

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Received September 20, 1955

Ukrainian Academy of Agriculture

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*T. p. = C. B. Translation pagination.

ALKYLATION OF BENZENE WITH POLYHALOGENATED DERIVATIVES IN PRESENCE OF METALLIC ALUMINUM

K. I. Porshakova, N. G. Sidorova and I. P. Tsukervanik

The employment of metallic aluminum for the alkylation of aromatic hydrocarbons with monohalogenated derivatives and olefins was described in previous communications [1,2]. Continuing the investigation in this direction, we studied the condensation of benzene with 1,2-dichloroethane and chloroform. In presence of $AlCl_3$ these reactions are known to proceed differently under different conditions. It was of interest to establish the effect of the conditions upon the course of the reaction in presence of aluminum.

Many authors have studied the condensation of 1,2-dichloroethane with benzene in presence of aluminum chloride. Silva [3] reported the formation of 1,2-diphenylethane and a minor amount of ethylbenzene; Klebansky and Mironenko [4] obtained products of polycondensation (resin) together with a small quantity of 1,2-diphenylethane; Korshak and co-workers [5-7] showed that, depending upon the conditions, the main product is either a resin or 1,2-diphenylethane together with an insignificant amount of bis-[p-(β-phenylethyl)]-benzene. Similar results were obtained by Dolgov and Larin [8] with Radzievanowski's $AlCl_3$ ($AlCl_3$-P); a small amount of liquid fraction was isolated which the authors assumed to be 1,1-diphenylethane. The usual products of condensations of chloroform with benzene in presence of $AlCl_3$ are diphenylmethane and triphenylmethane [9-14]. In addition, in individual cases the formation has been reported of tetraphenylethylene [10], 9-phenylfluorene [12], triphenylchloromethane [13] and triphenylmethyl and its peroxide [14]. Condensation of chloroform with toluene gave, apart from the usual products, dimethylanthracenes [15,16]. With $AlCl_3$-P the main product of reaction is diphenylmethane [17,18], while with a mixture of metallic aluminum and antimony the main product is triphenylmethane [17].

TABLE 1

Results of Condensations of 18 g 1,2-Dichloroethane

Molar ratios of $C_2H_4Cl_2 : C_6H_6 : Al$	Duration of heating at 80° (in hours)	Yields of products	
		1,2-diphenylethane (%)	resin (in g)
1 : 4 : 0.1	1	39	13
1 : 4 : 01	2	40	13
1 : 4 : 0.1	3	41	13
1 : 4 : 0.1	5	39	13
1 : 4 : 0.06	2	41	13
1 : 4 : 0.02	2	44	13
1 : 4 : 0.01	2	15	12
1 : 10.6 : 0.06	2	71	7
1 : 14.2 : 0.06	2	68	7
1 : 10.6 : 0.4	2	67	8
1 : 2.1 : 0.06	2	13	18
1 : 1.4 : 0.06	2	—	resin

We performed condensations of benzene with 1,2-dichloroethane and chloroform under various conditions; the effect of the amount of aluminum and benzene and of the duration of heating were studied. Commencement of the reaction and its later continuation required heating of the mixture at 80°. Reaction of chloroform with benzene started after 5-15 minutes and continued at first very violently, and later with moderate intensity. In condensations of 1,2-dichloroethane with benzene, however, the reaction did not start even after prolonged heating; a small amount of butyl chloride was therefore added as a priming agent to start the reaction.

In later condensations 1,2-diphenylethane or a resin were obtained (depending upon the conditions), as well as a small amount of bis-[p-(β-phenylethyl)]-benzene and ethylbenzene, the same products as were obtained with $AlCl_3$ (Table 1). The consumption of aluminum in these reactions is small (only 0.02-0.06 g-atom per mole dichloroethane).

The ratio of benzene to dichloroethane has a considerable influence on the course of reaction: with a large excess of benzene, 1,2-diphenylethane is obtained (71% of the theoretical), while with a small amount of benzene only a benzene-insoluble resin is formed. Treatment of the resin remaining after distillation of the 1,2-diphenylethane gave, in some experiments, bis-[p-(β-phenylethyl)]-benzene with m.p. 91-91.5° and a crystalline product which did not melt sharply even after numerous recrystallizations.

Condensations of chloroform with benzene in presence of metallic aluminum were conducted with variations in the amounts of catalyst and benzene and in the duration of the reaction. Depending upon the conditions, the main products of reaction were triphenylmethane and diphenylmethane, together with a minute amount of anthracene (Table 2).

TABLE 2

Results of Condensation of Chloroform with Benzene[*]

Molar ratios of $CHCl_3 : C_6H_6 : Al$	Duration of heating at 80° (hours)	Yields of products		
		triphenylmethane (%)	diphenylmethane (%)	resin (in g)
1 : 11.3 : 0.11	3	40	10	7
1 : 11.3 : 0.11	6	37	—	—
1 : 11.3 : 0.11	10	38	11	8
1 : 11.3 : 0.02	3	20	4	3
1 : 11.3 : 0.22	3	17	32	4
1 : 11.3 : 0.65	3	—	33	5
1 : 11.3 : 0.65	6	—	50	5
1 : 15.1 : 0.11	3	40	—	—
1 : 20.4 : 0.11	3	42	6	6
1 : 30.9 : 0.22	3	35	35	1
1 : 0.2 : 0.01	6	7	—	18

The yields of triphenylmethane and diphenylmethane vary markedly with the amount of aluminum present. With a small amount of aluminum (0.1 g-atom per mole chloroform) the main product (up to 40%) is triphenylmethane; with a larger amount of aluminum (0.65 g-atom per mole chloroform) up to 50% diphenylmethane is obtained. In the latter case, anthracene was isolated from the resin. In similar condensations in presence of $AlCl_3$-P, Dolgov and co-workers obtained diphenylmethane (up to 40%) and only a little triphenylmethane (3-4%).

Diphenylmethane may be formed by reduction of diphenylchloromethane [8]

$$(C_6H_5)_2CHCl \xrightarrow{2H} (C_6H_5)_2CH_2 + HCl$$

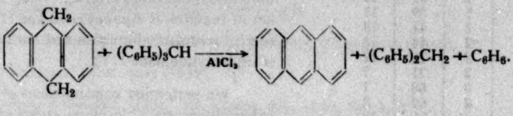
or by cleavage of triphenylmethane

$$(C_6H_5)_2CHC_6H_5 \xrightarrow{HH} (C_6H_5)_2CH_2 + C_6H_6$$

at the expense of the hydrogen liberated during interaction of hydrogen chloride with metallic aluminum. A second source of hydrogen is the formation of anthracene from diphenylmethane according to the scheme proposed by Radzievanowski [19]:

$$C_6H_5CH_2C_6H_5 + HCl \longrightarrow C_6H_6 + C_6H_5CH_2Cl,$$
$$2C_6H_5CH_2Cl \longrightarrow 2HCl + C_{14}H_{10} + H_2.$$

We consider a reaction of concomitant hydrogenation-dehydrogenation to be probable:



EXPERIMENTAL

The starting substances required for the condensations were thoroughly dried and distilled. Metallic aluminum was rubbed down with a file, quickly weighed and placed in the reaction flask with a small quantity of benzene.

Condensations were performed in the same apparatus as for the reactions of monohalogenated derivatives with aromatic hydrocarbons [1]. Condensations of benzene with 1,2-dichloroethane were performed in the following manner: in a reaction flask were put benzene (20 g) and metallic aluminum and then butyl chloride (0.5 g) as a priming agent to start the reaction. After the reaction had started, a mixture of dichloroethane and benzene was added in one portion or dropwise from a dropping funnel; after this operation the reaction sometimes stopped entirely or slowed down and only started again after prolonged heating (3-4 hours). Usually, however, copious separation of yellow froth and hydrogen chloride started after 15-20 minutes and ceased after about an hour; after this, heating was continued for 1-5 hours. The reaction mixture was left until the following day, then decomposed with water and acidified with hydrochloric acid. The benzene layer was separated, washed with water, dried over $CaCl_2$ and fractionated. In Table 1 are set forth the results of these condensations. In all the experiments, apart from the two last ones, a small amount of ethylbenzene with b.p. 134-136° (730 mm) was obtained. 1,2-diphenylethane came over at 135-137° (10-11 mm), m.p. 52°.

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[*] In the first nine experiments the amount of chloroform was 20 g; in the tenth it was 10 g, and in the last one it was 160 g.

After distillation of the 1,2-diphenylethane, the resin in some experiments was fractionated in vacuum (3-4 mm) and gave two fractions: 1) b.p. 175-185°, 2) b.p. 185-240°.

From the first fraction a colorless crystalline substance was isolated and had m.p. 91-91.5° after ten recrystallizations from alcohol. This substance corresponds to bis-[p-(β-phenylethyl)-benzene, isolated by Korshak and co-workers [7].

From the second fraction a colorless crystalline substance was likewise separated; it melted at above 100° but did not have a sharp melting point. The residue after distillation of these substances was only a minute amount of resin. With approximately equimolar ratio of benzene to dichloroethane, a benzene-insoluble resin was obtained which was not subjected to fractionation.

Benzene was condensed with chloroform in the absence of a priming agent; the reactants were placed in the flask and heated to the boiling point of benzene, and an energetic reaction commenced after 10-30 minutes. When using larger amounts of metallic aluminum (1-3 g), the reaction went so violently that external cooling of the flask with cold water was necessary. The reaction was brought to an end by heating the mixture at 80° (3-10 hours). The mixture was afterwards left until the next day and worked up by the usual procedure. Results of the condensations are set forth in Table 2. The main products are triphenylmethane, diphenylmethane and a resin. The diphenylmethane was distilled from a flask with a column at 132-135° (13-15 mm). After recrystallization from alcohol, it melted at 26-27°. After the diphenylmethane had been distilled off, the contents of the flask were transferred to a special Wurtz flask with a wide side tube for distillation of the triphenylmethane. The latter came over at 356-359° (730 mm) or at 197-200° (5-6 mm). Pure triphenylmethane, recrystallized from alcohol, melted at 92-93°.

When the reaction had been performed with a large amount of aluminum, the distillation of the resin remaining after removal of the triphenylmethane yielded anthracene at above 359° (730 mm). After three recrystallizations from alcohol it melted at 214°.

SUMMARY

1. The interaction of 1,2-dichloroethane and chloroform with benzene in presence of aluminum was studied.

2. It was shown that condensation of 1,2-dichloroethane with benzene goes in a manner similar to the corresponding reaction in presence of $AlCl_3$. In addition to the diphenylmethane and triphenylmethane usually formed on condensation of chloroform with benzene in presence of $AlCl_3$, anthracene was obtained. The amount of the latter increases with increasing yield of diphenylmethane.

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Received June 23, 1955

University of Central Asia and Central
Asian Institute of Technology

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*T.p. = C. B. Translation pagination.

REACTION OF ORGANIC BASES WITH METALLIC SALTS

IV. REACTION OF ANTIPYRINE WITH THIOCYANATES OF ZINC AND CADMIUM

S. E. Burkat

In the preceding paper [1] we showed that antipyrine reacts with thiocyanic acid to form a salt $C_{11}H_{12}ON_2 \cdot HCNS$; in an acid medium it reacts with cobalt thiocyanate to form the complex $(C_{11}H_{12}ON_2)_2 \cdot H_2[Co(CNS)_4] \cdot 2C_{11}H_{12}ON_2$. An entirely different type of thiocyanate complexes of antipyrine was described by D. I. Ryabchikov and E. A. Terentyeva [2] for the rare metals, and by T. E. Gulyaeva [3] for aluminum, iron (3^+) and chromium, while Kaufman [4] described a molecular compound of antipyrine with strontium thiocyanate of the composition $6C_{11}H_{12}ON_2 \cdot Sr(CNS)_2$. We have not found any data for possible complexes of antipyrine with thiocyanates of other metals in the literature accessible to us.

In the present paper we describe the results of investigation of the products of interaction of antipyrine with thiocyanates of zinc and cadmium. The experiments showed that compounds poorly soluble in water are formed; the composition and properties vary according to the reaction of the medium. Thus, in addition to an aqueous solution of antipyrine of a complex zinc or cadmium thiocyanate, precipitates are formed whose composition may be expressed by the schematic formula $2\,Ant \cdot Me(CNS)_2$ (I), where $Ant = C_{11}H_{12}ON_2$, and $Me = Zn, Cd$. The process of formation of these compounds may be represented by the following equation:

$$2Ant + Me^{2+} + 2CNS' = 2Ant \cdot Me(CNS)_2.$$

In an acid medium antipyrine reacts with zinc and cadmium thiocyanates to form complexes of another composition, corresponding to the general formula $(Ant)_2H_2[Me(CNS)_4] \cdot 2\,Ant$ (II). Unlike compounds of type (I), the complexes (II) possess a very pronounced acidic character and titrate with caustic alkali. Formation of complexes (II) may be represented by the following equation:

$$4Ant + 2H^{\cdot} + Me^{2+} + 4CNS' = (Ant)_2H_2[Me(CNS)_4] \cdot 2Ant.$$

On adding cadmium thiocyanate to a solution of antipyrine in an acetic acid medium, we can observe the nearly simultaneous formation of complexes of types (I) and (II): at the start a resin-like complex (II) separates from solution; after the solution has then stood for a short period, a white crystalline precipitate of complex (I) comes down. Boiling of the resinous complex with water leads to its partial conversion into complex (I), as is evident from the formation of a white crystalline precipitate when the solution is cooled. This process may be represented by the following equation:

$$(Ant)_2H_2[Me(CNS)_4] \cdot 2Ant \rightleftarrows 2Ant \cdot Me(CNS)_2 + 2Ant + 2H^{\cdot} + 2CNS^-.$$

In aqueous solutions of the prepared compounds of antipyrine with zinc and cadmium thiocyanates, the presence of an organic base, a metal and thiocyanate ion, is easily established by the usual methods. The compounds obtained are listed in the table.

Formula	Melting point
$(C_{11}H_{12}ON_2)_2H_2[Zn(CNS)_4] \cdot 2C_{11}H_{12}ON_2$	50— 52°
$2C_{11}H_{12}ON_2 \cdot Zn(CNS)_2$	70— 72
$(C_{11}H_{12}ON_2)_2H_2[Cd(CNS)_4] \cdot 2C_{11}H_{12}ON_2$	78— 80
$2C_{11}H_{12}ON_2 \cdot Cd(CNS)_2$	202—204

EXPERIMENTAL

Preparation of antipyrinium tetrathiocyanozincate. 3.75 g antipyrine is dissolved in 50 ml 0.5 N hydrochloric acid and to the resultant liquid a solution of 1.5 g crystalline zinc sulfate $ZnSO_4 \cdot 7H_2O$ and 5 g ammonium thiocyanate in 20 ml water are added with stirring. The resinous precipitate is pressed to remove liquid, washed 2-3 times with cold water, then 2-3 times with boiling water (10 ml portions), and dried at 80°. Yield of product 85% reckoned on the antipyrine taken into reaction.

A vitreous brownish-yellow mass, transparent and nearly colorless in a thin layer. At 15° the solubility in water is 0.07%. The aqueous solution is colorless. The substance dissolves in caustic alkalies, in ammonia, in ethyl alcohol and in chloroform.

Found %: Zn 5.94, 6.06; CNS' 22.80, 23.31; antipyrine 72.20, 73.00. $(C_{11}H_{12}ON_2)_2$ $H_2[Zn(CNS)_4] \cdot$ $\cdot 2C_{11}H_{12}ON_2$. Calculated %: Zn 6.21; CNS' 22.06; antipyrine 71.73.

Preparation of diantipyrine zinc thiocyanate. 2.9 g crystalline zinc sulfate $ZnSO_4 \cdot 7H_2O$ and 3 g ammonium thiocyanate are dissolved in 20 ml water and the resultant liquid is run with stirring into a solution of 3.8 g antipyrine in 20 ml water. The resultant resinous mass is separated from the liquid and dried at 80°. Yield 95% reckoned on the antipyrine taken into reaction. The product is washed 2-3 times with cold water, then 2-3 times with boiling water (separate portions of 10 ml each), and dried at 80°. A pale amber-colored vitreous mass. At 15° the solubility in water is 0.33%. The product dissolves in caustic alkalies, ammonia and ethyl alcohol; it is partly soluble in chloroform.

Found %: Zn 11.52, 11.89; CNS' 21.12, 21.26; antipyrine 68.56, 67.98. $2C_{11}H_{12}ON_2 \cdot Zn(CNS)_2$. Caculated %: Zn 11.71; CNS' 20.81; antipyrine 67.48.

Preparation of antipyrinium tetrathiocyanocadmiate. 3.8 g antipyrine is dissolved in 50 ml 0.25 N hydrochloric acid; a solution of 4 g crystalline cadmium nitrate $Cd(NO_3)_2 \cdot 5H_2O$ and 4 g ammonium thiocyanate in 20 ml water is then stirred into the liquid. The resinous precipitate is separated from the liquid, washed 2-3 times with cold water, then 2-3 times with boiling water (separate 10 ml portions), and dried at 80°. Yield 80% reckoned on the antipyrine taken into reaction.

Pale yellow vitreous mass. The solubility in water at 15° is 0.36%. Soluble in ammonia, ethyl alcohol and chloroform.

Found %: Cd 11.20, 10.42; CNS' 21.40, 21.76; antipyrine 67.82, 68.33. $(C_{11}H_{12}ON_2)_2[Cd(CNS)_4] \cdot$ $\cdot 2C_{11}H_{12}ON_2$. Calculated %: Cd 10.24; CNS' 21.16; antipyrine 68.80.

Preparation of diantipyrine cadmium thiocyanate. 6.2 g crystalline cadmium nitrate $Cd(NO_3)_2 \cdot 4H_2O$ and 6.2 g ammonium thiocyanate are dissolved in 20 ml water, and a solution of 3.8 g antipyrine in 20 ml water is stirred into the liquid. The precipitate is collected on a glass filter, washed with 10-15 ml cold water, thoroughly suction-filtered, and dried at 90°. Yield 90% reckoned on the antipyrine taken into reaction. The product is twice crystallized from boiling water (the first time from 120 ml and the second from 50 ml) and dried at 90°.

A fine crystalline, white powder. The solubility in water at 15° is 1.60%. It dissolves in ammonia and ethyl alcohol, and in part in chloroform.

Found %: Cd 20.12, 20.42; CNS' 21.40, 20.67; antipyrine 60.78, 60.21. $2C_{11}H_{12}ON_2 \cdot Cd(CNS)_2$.
Calculated %: Cd 18.5; CNS' 19.19; antipyrine 62.24.

SUMMARY

1. Antipyrine forms compounds with zinc and cadmium thiocyanates which are sparingly soluble in water.

2. Depending upon the reaction of the medium in which the interaction takes place, antipyrine forms two types of compounds with each of the salts in question; their composition may be represented by the schematic formulas $2\,Ant \cdot Me(CNS)_2$ and $(Ant)_2H_2[Me(CNS)_4] \cdot 2\,Ant$.

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Received May 19, 1955

State Institute of Medicine

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*T.p. = C. B. Translation pagination.

HYDROGENATION OF SOLUTIONS OF BUTADIENE RUBBER AT ATMOSPHERIC PRESSURE AND ROOM TEMPERATURE

I. PREPARATION OF RUBBERS OF DIFFERENT DEGREES OF HYDROGENATION, STUDY OF THEIR PROPERTIES

A. I. Yakubchik and G. N. Gromova

Study of the chemical structure of butadiene polymers, their chemical reactions and the properties of their transformation products throws light upon the relation between their chemical structure and some chemical, physical and physicomechanical properties. By means of the ozonolysis method the influence of certain factors (nature of the alkali metal, temperature and method of polymerization) upon the structure of the butadiene polymer was determined. More particularly, the percent of butadiene groupings in the 1,4 and 1,2 positions was established [1-4]. It was found that an increase in the rubber of the content of butadiene groupings polymerized in the 1,4-position favorably influenced its technically valuable properties.

In the present paper we submit the results of investigation of the process of hydrogenation of one of the synthetic butadiene rubbers.

Work on rubber hydrogenation in the past has been mainly carried out on natural rubber and the main objective was the elucidation of its structure [5-10]. Hydrogenation of rubber was effected over metal catalysts, at various temperatures, in the mass and in solution in methylcyclohexane, hexahydrotoluene and ethyl ether. Depending upon the conditions of hydrogenation, hydrorubbers of various molecular weights were obtained. Hydrorubbers obtained at 270° differed from those obtained at 100° and lower in always having a lower molecular weight and, as a rule, they did not possess elastic properties. Later it was shown that this phenomenon is associated with destruction of the rubber molecules at elevated temperature [11-13]. Hydrorubbers with molecular weights of 70-80 thousand were obtained by hydrogenation of rubber in dilute solutions of 50-100°.

An investigation of the properties of hydrogenated rubber, and in particular of its viscosity, specific gravity and refractive index revealed that the material in most cases contains products of decomposition and cyclization. If breakdown of the rubber does not occur during the process of hydrogenation, the viscosity of solutions of natural rubber does not alter and the refractive index falls. Cyclization leads to a rise in the refractive index of hydrogenated natural rubber. After our study was completed, an announcement appeared of the production of new rubber-like products ("hydropols") possessing a series of valuable properties and obtained by hydrogenation of emulsified polybutadiene [15].

The objectives of the present investigation were: 1) clarification of the possibility of selective hydrogenation of the double bonds in butadiene rubber and 2) clarification of the relation between the number and character of the double bonds in rubber molecules on the one hand, and some of its properties on the other hand. It is known that butadiene rubber contains olefinic bonds with different degrees of substitution, namely, mono- and disubstituted. On the basis of the studies of S. V. Lebedev [16], it was to be expected that the curve of rate of hydrogenation of butadiene rubber would have a discontinuity and that this curve could serve for calculation of the number of double bonds with different degrees of substitution. The butadiene rubber selected for this investigation contained 56.6% external double bonds and had good solubility.

EXPERIMENTAL

Purification of the Rubber, Preparation of Catalysts and Procedure for Hydrogenation of Rubber in Solutions

Preliminary removal of impurities from the butadiene rubber (treated with 2% neozone D) was effected by three precipitations of a 1-1.5% benzene solution with ethyl alcohol; the rubber was then dried to constant weight at 30-35° and a residual pressure of 2-3 mm. Purification and drying of the rubber were effected in an atmosphere of pure nitrogen [17]. The alcohol and benzene were carefully purified. Thiophene-free benzene was used. Hydrogenation of rubber solutions was performed in presence of palladium precipitated on calcium carbonate and on nickel, platinum black (from platinum oxide), platinized carbon (activated with chloroplatinic acid), and Raney nickel.

Catalysts were prepared in the following manner. Palladium on calcium carbonate was prepared by Busch's method [18]. Reduction of palladium hydroxide by hydrogen was carried out in heptane just before experiment. 1 g catalyst contained 0.0122 g palladium. Palladium on freshly reduced nickel was prepared by Ginzberg's method [19]. Freshly reduced nickel was obtained by reduction of nickel oxide at 280-330° in an atmosphere of electrolytic hydrogen. The hydrogenation catalyst was employed in the dry form. 1 g catalyst contained 0.0377 g palladium. Platinum black was prepared from platinum oxide by Adams' method [20]. The platinum oxide was reduced with hydrogen in alcohol immediately before an experiment. 1 g platinum oxide contained 0.795 g platinum. Platinized carbon, activated with chloroplatinic acid, was obtained by Zelinsky's method [21]. The platinized carbon was activated with chloroplatinic acid just before an experiment. 1 g of platinized carbon contained 0.0867 g platinum. Raney nickel was prepared by the Adkins method [22].

The activity of each of the above catalysts and the suitability of the solvent were tested on allyl alcohol and eugenol which had the following characteristics:

Allyl alcohol, b.p. 95.5-96°, n_D^{20} 1.4125; eugenol, b.p. 110.5-111° (3mm), n_D^{20} 1.5408.

Hydrogenation of rubber in solutions at atmospheric pressure was performed in the apparatus of S. V. Lebedev [2], using a glass "duck" with a capacity of 500 ml at 20 ± 0.2°. The solvents used for the rubber were saturated hydrocarbons (heptane and hexane) and the concentration of the solution for hydrogenation did not exceed 0.8%. Hydrogen for the hydrogenation was prepared by electrolysis of a 30% sodium hydroxide solution. Readings of the amount of hydrogen absorbed were taken every $^1/_2$ minute with an accuracy of ± 0.25 ml.

The hydrocarbons used as solvents had the following characteristics:

Heptane, b.p. 98.3°, n_D^{20} 1.3879, d_4^{20} 0.6839, content of unsaturated hydrocarbons and sulfur nil, octane number 0.0; hexane b.p. 68.8°, n_D^{20} 1.3758, d_4^{20} 0.6596, bromine number 0.1.

Determination of Influence of Some Factors Upon the Rate of Hydrogenation of Rubber Solutions

With the objective of finding the optimum conditions for hydrogenation of rubber, a study was made of the effect of intensity of stirring, of the amount of catalyst and of the concentration of the rubber solution (at constant rubber/catalyst ratio) on the rate of hydrogenation of rubber solutions. The volume of test solution was 200 ml. Results of the investigations over palladium on calcium carbonate are presented in Figs. 1-3.

The data show that the rate of hydrogenation of rubber solutions does not depend upon the intensity of stirring within the range of 240 to 450 revolutions per minute. The amound of catalyst has a considerable influence upon the rate of hydrogenation of rubber solution (Fig. 2) which rises appreciably with increasing amount of catalyst to 4 and 8 times the original amount. Finally, the rate of rubber hydrogenation is substantially independent of the concentration of the solution in the range of 0.2 to 0.8% when the rubber/catalyst ratio is maintained at 1:10 and 1:20 (Fig. 3). We see from the results of Figs. 2 and 3 that the attainment of far-reaching hydrogenation of rubber in solutions of 0.2-0.8% concentration necessitates the use of palladium on calcium carbonate catalyst in such quantity that the rubber/catalyst ratio is not less than 1:20.

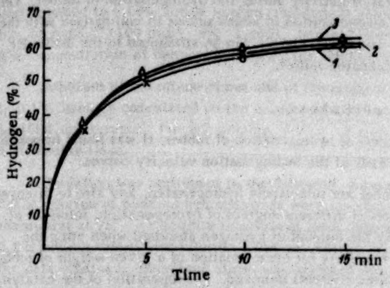

Fig. 1. Influence of intensity of stirring on the extent of hydrogenation of butadiene rubber over palladium on calcium carbonate catalyst.
Intensity of stirring (revolutions per minute): 1) 240, 2) 350, 3) 450.

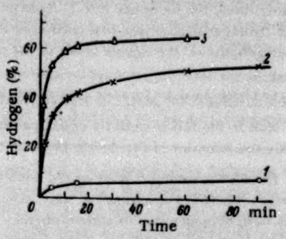

Fig. 2. Influence of amount of palladium on calcium carbonate catalyst on the extent of hydrogenation of rubber solution.
1) 2 g, 2) 8 g, 3) 16 g.

It is noteworthy that the form of the curve of hydrogenation velocity is identical in all cases regardless of the conditions of hydrogenation, when using palladium on calcium carbonate as catalyst. In each case the curve quickly flattens. A similar picture is observed with all the catalysts that we investigated. Fig. 4 contains the curves of hydrogenation velocities of rubber over two different palladium catalysts; in the first case (1) the amount of palladium is 3 times smaller than in the second (2).

The abrupt flattening of the hydrogenation velocity curve might be associated with the difficulty of hydrogenation of the double bonds in the partially hydrogenated rubber and by the declining activity of the catalyst during hydrogenation. An examination was therefore made of the effect of addition of fresh amounts of catalyst and of rubber on the hydrogenation velocity in presence of palladium on calcium carbonate. In the graphical representation we plotted the duration in minutes on the abscissas against the amount of hydrogen absorbed (in milliliters) in separate intervals of time. Results are shown in Fig. 5 and 6.

The sharp rise in hydrogenation velocity when using freshly reduced catalyst in comparison with the velocity at which the preceding process of hydrogenation had been terminated (Fig. 5), as also the considerable fall

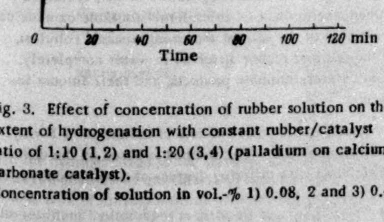

Fig. 3. Effect of concentration of rubber solution on the extent of hydrogenation with constant rubber/catalyst ratio of 1:10 (1,2) and 1:20 (3,4) (palladium on calcium carbonate catalyst).
Concentration of solution in vol.-% 1) 0.08, 2 and 3) 0.4.

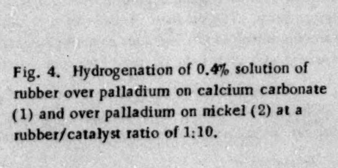

Fig. 4. Hydrogenation of 0.4% solution of rubber over palladium on calcium carbonate (1) and over palladium on nickel (2) at a rubber/catalyst ratio of 1:10.

in rate of hydrogenation of the second added amount of rubber as compared with the initial rate of hydrogenation of the first portion of rubber (Fig. 6) indicate a fall in catalyst activity during the hydrogenation of rubber. On the other hand, the increased rate of hydrogenation of the second portion of added rubber in comparison with the rate of hydrogenation of the first portion at the end of the first stage (Fig. 6) can be attributed to the difficulty of hydrogenation of the double bonds in the partially hydrogenated rubber.

Separation and Investigation of Hydrogenated Rubber

Due to the fall in activity of the catalysts in the process of hydrogenation of rubber, it was found impossible to study the behavior of the double bonds in rubber on the basis of the hydrogenation velocity curves.

In order to establish whether the double bonds in rubber are selectively hydrogenated, and also to discover the relation between structure and some properties of rubbers of different degrees of hydrogenation, solutions of rubber were hydrogenated to various degrees as indicated by the amount of hydrogen absorbed when using the same catalysts. After addition of the amount of hydrogen necessary for hydrogenation of a given weight of rubber to a given extent, the "duck" was purged with nitrogen and the contents removed. For separation of the catalyst, the solution of the products of hydrogenation of rubber were centrifuged at 2,500-3,000 r.p.m. The main part of the solvent was then distilled off at 30-35° and a pressure of 100-60 mm. Hydrogenated rubber was precipitated from the residual solution with purified ethyl alcohol and dried to constant weight at 30-35° and a pressure of 2-3 mm.

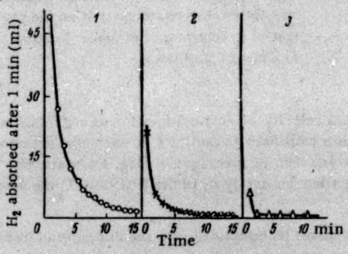

Fig. 5. Effect of fresh additions of catalyst on the rate of hydrogenation of rubber solution (catalyst: palladium on calcium carbonate).
Portions of catalyst: 1) 1st, 2) 2nd, 3) 3rd.

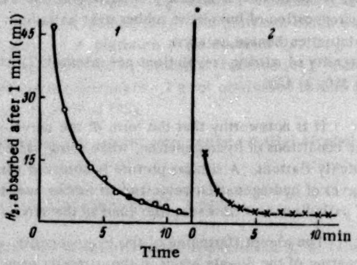

Fig. 6. Effect of fresh portions of rubber on the rate of hydrogenation of rubber solution (catalyst: palladium on calcium carbonate).
Portions of rubber: 1) 1st, 2) 2nd.

The original and the hydrogenated rubber were analyzed for total unsaturation, content of external and internal double bonds, refractive index, relative viscosity of the benzene solutions (same percent of substance) and temperature of vitrification.

Total unsaturation was determined with iodine bromide solution [24,25]. The content of outer double bonds was determined by ozonolysis [2]. The ozonide obtained by ozonization of rubber in chloroform had the form of a white, gelatinous mass; after distillation of the solvent (15-18 mm) at a bath temperature of 20°, it formed a white, friable powder. When hydrogenated rubber was ozonized, the amount of chloroform-insoluble ozonide decreased with increasing degree of hydrogenation, and after removal of the solvent the ozonide was a colorless, syrupy mass. The products of breakdown of the ozonides of the original rubber dissolved in water completely. Decomposition of the ozonides of the hydrogenated rubber gave water-insoluble products, and their amount increased with increasing degree of hydrogenation of the rubber.

We determined the content of outer double bonds by comparing the curves of rate of oxidation of 1-vinylcyclohexene-3 and of the investigated sample with benzoyl hydroperoxide. The method is based on the differing rate of oxidation with benzoyl hydroperoxide of an olefinic bond with differing degrees of substitution [26-28].

The benzoyl peroxide, recrystallized from alcohol, had m.p. 103-103.5°. Its purity was 99.2-99.5%, which corresponded to 6.56% active oxygen (theoretical value 6.61%). 1-vinyl-cyclohexene-3 (butadiene dimer) had b.p. 65.5-66.2° (100 mm), n_D^{20} 1.4601. Benzoyl hydroperoxide was prepared by N. A. Prilezhaev's method [26]. The concentration of benzoyl hydroperoxide solution was usually about 1% reckoned on the active oxygen.

Solutions of butadiene dimer and of the original and the hydrogenated rubber were prepared for oxidation in 0.1 N strength calculated on the consumption of halogen at the double bonds, assuming the original rubber to be 100% unsaturated. For this purpose, 0.27 g of each of the substances was dissolved in 100 ml chloroform in a measuring flask.

Oxidation was performed in the following manner: equal volumes of 0.1 N solution of the substance and 0.2 N solution of benzoyl hydroperoxide were run into a flask with vigorous shaking; the flask was then left in a thermostat at 25°. At definite intervals of time, samples were withdrawn from the flask and back-titrated with 0.1 N sodium thiosulfate solution. The percentage oxidation of the double bonds was calculated on the basis of the data obtained. Butadiene dimer was oxidized under similar conditions.

The refractive index of the rubber was determined in the Abbe refractometer at 20° [29]. The relative viscosity of 0.08% benzene solutions of the rubber was determined in the Ostwald viscometer at 25° [30]. The temperature of vitrification was determined in the apparatus of A. I. Marei [31].

Properties of Butadiene Rubbers with Varying Degrees of Hydrogenation

The results of investigation of the properties of butadiene rubbers of various degrees of hydrogenation, obtained with various catalysts, are presented in Table 1, from which we see that the unsaturation decreases with increasing extent of hydrogenation over palladium on nickel and over palladium on calcium carbonate; at the same time, the percentage content of outer and internal double bonds decreases. The fall in the ratio of outer double bonds (1,2) to internal double bonds (1,4) in rubber with increasing degree of hydrogenation points to the presence of a certain selectivity in the hydrogenation of the outer double bonds.

TABLE 1

Characteristics of Butadiene Rubber of Various Degrees of Hydrogenation Obtained with Different Catalysts

Catalyst	Percent hydrogen absorbed	Unsaturation (%)	Percent of double bonds		Ratio of double bonds in the 1,2 and 1,4 positions	n_D	Relative viscosity (of 0.08% benzene solution)	Temperature of vitrification
			outer (1, 2)	inner (1, 4)				
—	0	88.2	56.6	37.0	1.53	1 5120	1.247	–60.0°
Palladium on nickel	24.6	61.9	—	28.5	—	1.5005	1.228	–65.0
	29.2	56.5	36.2	26.5	1.36	1.4980	1.216	–66.0
	42.0	48.9	—	21.5	—	1.4910	1.203	—
	69.5	19.0	12.7	11.5	1.1	1.4860	1.180	–70.0
Palladium on $CaCO_3$	27.2	56.9	38.0	28.0	1.35	1.5000	1.224	–64.0
	54.1	33.3	20.4	19.0	1.07	1.4922	1.197	–66.4
	74.7	11.6	5.6	5.5	1.02	1.4836	1.163	–70.6
	86.3	4.1	—	—	—	1.4801	1.140	–70.5
Platinum black	5.0	85.2	—	—	—	1.5115	—	—
Platinized carbon + H_2PtCl_6	— *	35.5	—	17.0	—	1.4900	—	–67.0
Raney nickel	18.1	— **	50.1	35.5	1.41	—	1.247	–59.5
	42.6	72.7	46.4	34.5	1.35	—	1.29	–59.7
	66.2	—	—	25.5	—	—	—	—

*In the hydrogenation of the standard substances, allyl alcohol and eugenol, it was shown that with this catalyst it was impossible to quantitatively measure the hydrogen absorbed by the substance being hydrogenated.

**The lack of correspondence between the quantity of hydrogen absorbed by the rubber and the unsaturation of the resultant hydrorubber is difficult to explain at present.

Since there was substantially no hydrogenation of solutions of rubber in presence of platinum black, a sample of hydrogenated rubber with an unsaturation of 35.5% was obtained over platinized carbon activated by additions of chloroplatinic acid. Results of determination of the internal double bonds in the resultant sample of hydrorubber also indicate the absence of complete selectivity of hydrogenation of the double bonds in rubber. Some preference in the hydrogenation of outer double bonds in the rubber molecule was also observed over Raney nickel.

Thus, we see from the results of determination of the outer and inner double bonds in partially hydrogenated butadiene rubber, obtained with various catalysts, that the outer double bonds are hydrogenated at a greater rate than the inner bonds. A study of the properties of butadiene rubbers with various degrees of hydrogenation revealed a steady fall in the refractive index, a fall in the relative viscosity (0.08% solution in benzene) and a fall in the temperature of vitrification of rubber with increasing degree of hydrogenation. The fall in refractive index of the rubber with increasing degree of hydrogenation indicates the absence of cyclization, since otherwise the refractive index ought to have increased [9,11]. The fall in relative viscosity with increasing degree of hydrogenation of benzene solutions of butadiene rubber of equal concentrations might be a measure of the decomposition and change of form of the rubber molecules, i.e. of the change of chemical structure of the original rubber during the process of hydrogenation.

The temperature of vitrification of rubber is closely associated with its elasticity. According to the kinetic theory of elasticity [32], the energy of interaction between individual links of rubber, both along the chain and between individual chains, depends upon the chemical structure of the rubber. Our results on the hydrogenation of butadiene rubber show that the disappearance of the double bonds in the rubber molecule, associated with transformation of vinyl groups into ethylenic groups and with simultaneous diminution of the double bonds in the chain, leads to a fall in the energy of interaction between individual links which brings about a fall in the temperature of vitrification.

Determination of the Cause of the Fall in Relative Viscosity of Benzene Solutions During Hydrogenation

With the objective of establishing one of the possible causes of fall in relative viscosity of benzene solutions of rubber with increasing degree of hydrogenation, i.e. of the oxidative breakdown due to traces of oxygen in the system, the hydrogenation of rubber was effected over palladium on calcium carbonate in heptane under conditions of maximum exclusion of oxygen of the air both in the presence and absence of the antioxidant Neozone D (phenyl-β-naphthylamine). For this purpose, the solvent was twice fractionated in a nitrogen atmosphere and the transfer of the rubber solution from the ampoule to the "duck" was likewise effected under nitrogen. Neozone D was introduced into the purified rubber during its precipitation from benzene solution. The proportion of antioxidant was 2%. The properties of the resultant hydrorubbers are set forth in Table 2.

TABLE 2

Characteristics of Hydrogenated Butadiene Rubber Obtained with Palladium on Calcium Carbonate as Catalyst with Exclusion of Atmospheric Oxygen and in the Presence and Absence of the Antioxidant Neozone D

Rubber	Percent addition of hydrogen	Unsaturation (in %)	n_D	Relative viscosity (0.08% benzene solution)
—	0	86.2	1.5121	1.310
Purified	62.2	26.7	1.4905	1.253
Purified + 2% Neozone D	79.8	9.0	1.4838	1.248

These results show that the fall in viscosity also occurs in the absence of oxidative destruction (in presence of antioxidant). For clarification of the problem of the breakdown of rubber molecules during hydrogenation, determinations were made of the number average molecular weights and of the weight average molecular weights of the original and of the hydrogenated rubbers (Table 3).

TABLE 3

Results of Determination of the Average Molecular Weight of the Original Rubber and of the Rubber Hydrogenated in Presence of Palladium on Calcium Carbonate

Rubber	Unsaturation (in %)	Relative viscosity (0.08% benzene solution)	Average molecular weight	
			by weight	number
Original	86.2	1.310	715000	162000
Hydrogenated	2.0	1.180	715000	121000

The results in Table 3 show that the weight average molecular weight of butadiene rubber in the process of hydrogenation does not alter, thus indicating absence of breakdown of the high-molecular portion of the rubber. The insignificant breakdown of the low-molecular part of the rubber, reflected in the fall in the number average molecular weight of the rubber, cannot be the cause of the fall in viscosity of benzene solutions of the rubber due to hydrogenation. In order to account for this fall in viscosity, we must assume that the disappearance of the double bonds during hydrogenation leads to greater coiling of the molecule and consequently to a fall in the radius of its action in solution; in other words, the fall in viscosity of benzene solutions of butadiene rubber during hydrogenation is associated with a change of molecular form.

SUMMARY

1. Solutions of butadiene rubber were hydrogenated at atmospheric pressure and room temperature on the following catalysts: palladium on calcium carbonate, palladium on nickel, platinum black from platinum oxide, platinized carbon activated with platinic acid, and Raney nickel.

2. It was established that during hydrogenation on these catalysts the activity of the catalyst falls, due evidently to obstruction of their surface by the products of hydrogenation. It was therefore impossible to investigate the behavior of the double bonds in butadiene rubber on the basis of the hydrogenation rate curves.

3. Specimens of butadiene rubber of different degrees of hydrogenation were prepared over all the catalysts mentioned above, and the following determinations were made: total unsaturation, percent of inner and outer double bonds, refractive index, relative viscosity of 0.08% benzene solutions, and temperature of vitrification.

4. It was established that the outer bonds of the rubber are hydrogenated more rapidly than the inner bonds during hydrogenation over the above-mentioned catalysts.

5. It was established that with increasing degree of hydrogenation of butadiene rubber the refractive index falls, the relative viscosity of benzene solutions falls, and the temperature of vitrification becomes lower than that of the original rubber.

6. The fall in refractive index during hydrogenation points to the absence of cyclization and may be explained by the disappearance of the double bonds.

7. It is shown that the fall in viscosity of benzene solutions with progressive hydrogenation is associated with change in the form of the molecules of rubber.

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Received May 30, 1955

S. V. Lebedev All-Union Institute of Research
on Synthetic Rubber

THE IRREVERSIBLE CATALYTIC CONVERSION OF DIPENTENE OVER SKELETAL NICKEL IN THE LIQUID PHASE

G. L. Dranishnikov

The catalytic transformations of cycloolefinic hydrocarbons, known as irreversible catalysis, have been the subject of numerous investigations ever since these transformations were first observed by N. D. Zelinsky and N. L. Glinka [1]. The interest in irreversible catalysis was aroused by the great theoretical value of such chemical transformations and by the fact that the reactions of irreversible catalysis can be successfully applied to industrial syntheses of aromatic hydrocarbons and their various derivatives. In particular, the irreversible catalysis of terpenes is of considerable interest in connection with the great possibilities of production of synthetic fibers on the basis of polyesters of terephthalic acid which are easily obtainable by the oxidation of p-cymene. Cymene is, of course, one of the main products of irreversible catalysis of monocyclic terpenes of the series of p-menthane and of bicyclic terpenes which isomerize to monocyclic terpenes of the same series.

Many papers have been published on the irreversible catalysis of various compounds. A critical survey of these papers has been made by R. Ya. Levina [2]. A number of important regularities of irreversible catalysis were investigated with reference to the catalytic transformations of various terpenic hydrocarbons, in particular limonene (dipentene), terpinenes, terpinolene, α- and β-pinenes, and thujene. The main credit for this undoubtedly goes to N. D. Zelinsky and his school. In the overwhelming majority of investigations on irreversible catalysis of hydrocarbons, including terpenes, the catalysts used have been platina and palladium (on various supports or in the form of black), the high catalytic activity of which in irreversible catalytic reactions had already been observed by N. D. Zelinsky [3]. Considerably fewer papers are devoted to the study of other catalysts such as nickel, chromium oxide, molybdenum oxide, alumina, vanadium oxides (on supports and in the pure form), and active carbon [2,4]; in these studies the process took place predominantly in the vapor phase. In a study of the irreversible catalysis of monocyclic terpenes in the liquid phase, it was shown [5] that prolonged boiling in presence of a mixture of copper formate and nickel formate (metal ratio of 1:3) leads to irreversible transformation of the terpenes in such a manner that 3 moles of original terpene give 2 moles of p-cymene and 1 mole p-menthane. Using 2% of catalyst (on the weight of terpene), the process is completed in about 8 hours.

In recent years, both in research and industry, ever greater importance has been acquired by skeletal catalysts and, in particular, by skeletal nickel catalysts. The latter are used very successfully in reactions of hydrogenation, dehydrogenation, etc. [6]. The literature is lacking, however, in any reference to the possibility of their application in irreversible catalysis.

The present paper is a report of studies of the action of skeletal nickel catalyst in the liquid phase at atmospheric pressure and relatively low temperatures on dipentene, the susceptibility of which to irreversible vapor phase catalysis over palladized asbestos in a weak stream of carbon dioxide was demonstrated by N. D. Zelinsky [3]. Our data show that skeletal nickel in the absence of hydrogen quantitatively transforms dipentene, in the liquid phase at its boiling point, into a mixture of p-cymene and p-menthane: each 3 moles of dipentene yields 2 moles cymene and 1 mole menthane. The experiments also showed that the activity of skeletal nickel in the irreversible catalysis of dipentene is not inferior to such catalysts as platina and palladium, and that in respect of the facility and completeness of transformation, it is greatly superior to other catalysts. Thus, G. A. Rudakov and co-workers [4b] showed that the irreversible catalysis of dipentene over active carbon takes place at higher temperatures (420-450°) and is greatly complicated by a series of side reactions. Similar observations were made by S. R. Rafikov and co-workers [4d] on the irreversible catalytic conversion of dipentene over vanadium oxides.

Skeletal nickel also possesses undoubted advantages over the mixed catalyst proposed for the liquid-phase conversion of monocyclic terpenes [5]. With equal amounts of catalysts the process over skeletal nickel proceeds 4-5 times faster than over the mixed catalyst.

EXPERIMENTAL*

Dipentene was prepared by thermal isomerization of α-pinene [7] and was purified by two distillations in vacuum in a column (about 20 theoretical plates).

B.p. 71-72° (20 mm), d_4^{20} 0.843, n_D^{20} 1.4730. Did not possess optical activity. Literature data [8]: b.p. 71.5° (20 mm), d_4^{20} 0.8420, n_D^{20} 1.4725.

The catalyst was prepared by complete leaching with alkali of nickel-aluminum alloy, followed by numerous washings of the catalyst with water until it gave a neutral reaction to phenolphthalein. The prepared catalyst was stored under alcohol.

Catalytic experiments were carried out in a small three-necked round-bottomed flask with a reflux condenser through which passed a glass propeller-type stirrer with mechanical drive. Through one of the side tubes carbon dioxide gas was introduced to protect the terpene against autoxidation during the experiment; the second side tube served for measurement of the temperature of the reaction medium and for withdrawal of samples of catalyzate. The flask was heated on a sand bath. The rate of catalysis was checked by periodical withdrawal of samples of catalyzate and by their titration (for content of unreacted dipentene) with bromide-bromate mixture [9]. A series of experiments on the catalytic conversion of dipentene gave identical end results with 10-2% of catalyst. The only difference was in the rate of reaction. Two of them are described below – the first without measurement of the rate of reaction, the second with calculation of the rate of reaction.

Experiment 1. 97.0 g dipentene and 9.5 g catalyst (in the form of slurry) were put in the flask. The latter was placed on a sand bath (previously heated to 200°), the stirrer was at once started and a weak stream of carbon dioxide introduced through a side tube. For removal of the alcohol introduced with the catalyst, the second side tube was kept open until the temperature of the reaction mass reached 150°. The temperature in the flask then rose rapidly to 175° and was held at this level until the end of the experiment. Two hours after the temperature had reached 175°, the experiment was stopped. After standing and after separation of the catalyst, the catalyzate was perfectly transparent and colorless, n_D^{20} 1.4730 (the same as that of the original dipentene). Pleasant odor. The catalyzate did not decolorize bromine water.

Experiment 2. 57.2 g dipentene and 6.0 g catalyst were taken. Same reaction conditions. A sample of catalyzate, taken half an hour after the temperature had reached 175°, contained only 1.9% dipentene. After an hour the reaction stopped completely. In all its properties the catalyzate was identical with that in the first experiment.

Examination of catalyzates. This was effected by one and the same method and gave consistent results. Only the data of Experiment 2 are therefore reported. 20.0 ml (16.8 g) catalyzate was shaken 15 minutes with 30 ml sulfuric acid (d 1.84) in a graduated cylinder with a ground-glass stopper at a temperature of 70°. After standing and cooling, the contents of the cylinder formed two layers.

The upper layer (hydrocarbon) amounted to 6.8 ml (5.44 g). The hydrocarbon was collected, washed with sodium carbonate solution and then with water, dried with calcium chloride, and distilled over sodium from an Arbuzov flask. All the hydrocarbon came over at 169-170° (760 mm). The main portion came over at 169.5° (about 95%).

d_4^{20} 0.797, n_D^{20} 1.4398, MR_D 46.15; calc. 46.18. Literature data for p-menthane [10]: b.p. 169-170° (760 mm), n_D^{20} 1.4375, d_4^{20} 0.7929.

The lower (acid) layer was transparent and light-brown in color. When it was poured into concentrated hydrochloric acid, a sulfonic acid came down; hydrolysis of the latter by steam distillation [11] gave a hydrocarbon having n_D^{20} 1.4903 (10 ml or 8.7 g). After washing with sodium carbonate solution and water and drying with calcium chloride, the hydrocarbon was distilled over sodium from an Arbuzov flask. All the hydrocarbon came over at 176-178° (760 mm). The main portion (about 96%) distilled at 177.5°.

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*L. F. Tushina, K. E. Sosnina and F. M. Trubkina participated.

n_D^{20} 1.4898, d_4^{20} 0.855, MR_D 44.75; calc. 44.78. Literature data for p-cymene [12]: b.p. 177° (760 mm), n_D^{20} 1.4904, d_4^{20} 0.857.

Part of this hydrocarbon was oxidized with chromic mixture with heating and a good yield of acid with sublimation temperature of 300° was obtained.

Titration of 0.0974 g of the acid (in alcohol solution) consumed 12.06 ml 0.1 N sodium hydroxide. Theoretical requirement for $C_6H_4(COOH)_2$ is 11.74 ml.

Analysis of silver salt of the acid. 0.4326 g substance: 0.2360 g Ag. Found %: Ag 54.2. $C_8H_4O_4Ag_2$. Calculated %: Ag 54.0.

The physical properties, the titration results and the analysis of the silver salt show the acid to be terephthalic acid. This is further confirmation that the sulfuric acid-soluble part of the catalyzate is p-cymene. One of the samples of catalyzate was fractionated in vacuum in a column with a plate number of about 20. The results of fractionation confirmed the data of the chemical investigation and also showed that the catalyzate consists of p-cymene and p-menthane in 2:1 ratio.

SUMMARY

It was found that skeletal nickel is a highly active catalyst for N. D. Zelinsky's conversion reaction: in presence of skeletal nickel, dipentene in the liquid phase is quantitatively transformed into a 2:1 mixture of p-cymene and p-menthane.

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Received April 20, 1955

Archangel Institute of Wood Technology

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*T.p. = C. B. Translation pagination.

THE INCREASING COMPLEXITY OF THE CARBON SKELETON OF MOLECULES IN THE ACTION OF IODIDES ON HALOGENATED ORGANIC COMPOUNDS

B. V. Tronov and V. M. Aksenenko

It has been known for a long time that when iodides act upon organic compounds containing two atoms of chlorine or bromine at neighboring carbon atoms, free iodine is evolved and a double bond is formed instead of simple substitution of chlorine or bromine by iodine taking place:

$$\mathrm{RCHBr{-}CHBrR + 2NaI \rightarrow RCH{=}CHR + 2NaBr + I_2}.$$

In some cases iodine is also liberated in reaction with halogen compounds containing one atom of chlorine or bromine or two atoms of halogen at one group; in such cases the carbon skeleton undergoes doubling:

$$\mathrm{2(COOC_2H_5)_2CHBr + 2NaI \rightarrow (COOC_2H_5)_2CH{-}CH(COOC_2H_5)_2 + 2NaBr + I_2};$$

$$\mathrm{2(C_6H_5)_2CCl_2 + 2NaI \rightarrow (C_6H_5)_2CCl{-}CCl(C_6H_5)_2 + 2NaCl + I_2};$$

$$\mathrm{(C_6H_5)_2CCl{-}CCl(C_6H_5)_2 + 2NaI \rightarrow (C_6H_5)_2C{=}C(C_6H_5)_2 + 2NaCl + I_2}.$$

Finkelshtein [1] studied a series of such reactions and found that this transformation can be undergone by compounds in which the halogen is attached to a carbon which is also linked to two electronegative atoms or groups. A paper by B. V. Tronov and A. S. Samarin [2] draws attention to still another course of the reaction. The action of sodium iodide on chloromalonic ester led to formation of two products – the expected ethanetetracarboxylic ester and an ethylenetetracarboxylic ester $\mathrm{(COOC_2H_5)_2C{=}C(COOC_2H_5)_2}$.

With the objective of clarifying the mechanism of the action of iodides on organic halogen derivatives, we instituted experiments with many compounds possessing a sufficiently active halogen. We used benzyl chloride, o-nitrobenzyl chloride, chloro- and bromoacetophenones, ethyl chloroacetate, β-bromoethyl acetate, chloro- and bromobenzyl cyanides, the ethyl esters of phenylchloroacetic and phenylbromoacetic acids, α-chloro-, α-bromo- and α-iodoacetoacetic esters, γ-bromoacetoacetic ester. These compounds were subjected to the action of sodium iodide at room temperature or with heating on a water bath. With the first six compounds, only replacement of chlorine or bromine by iodine took place. Even such reactive substances as chloroacetophenone and bromoacetophenone only gave iodoacetophenone, which did not react further with NaI. Chloro- and bromobenzyl cyanide reacted quantitatively with doubling of the skeleton:

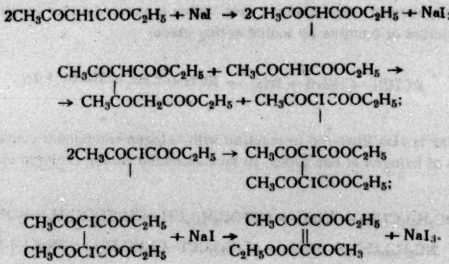
$$\mathrm{2C_6H_5CHClCN + 3NaI \rightarrow (C_6H_5CHCN)_2 + 2NaCl + NaI_3}.$$

Esters of phenylchloroacetic and phenylbromoacetic acids gave the ester of diphenylsuccinic acid. The ester of phenyliodoacetic ester (prepared by us) also behaved in the same manner. This last fact supported the hypothesis, advanced earlier, that organic chlorides and bromides in reaction with iodide salts at first change into the corresponding iodine compounds which then lose iodine under the action of the I^- ion:

$$2C_6H_5CHICOOC_2H_5 + NaI \rightarrow (C_6H_5CHCOOC_2H_5)_2 + NaI_3.$$

The cause of the cleavage of iodine is consequently the energy of formation of the complex anion I'_3.

Halogen derivatives of acetoacetic ester reacted in a complex manner. α-Halosubstituted derivatives gave unsaturated compounds as the main product, i.e. not only halogen but also hydrogen split off in this case from the same grouping, with formation of diacetylfumaric ester. Iodoacetoacetic ester here reacted in the same way as the chloro- and bromo- derivatives. A possible explanation of the cleavage of hydrogen halide is that the product of cleavage of halogen, for example ethanetetracarboxylic ester or diacetylsuccinic ester, is thereupon iodinated and next loses the two atoms of iodine located at adjacent groups. However, as special experiments showed, ethanetetracarboxylic ester is not susceptible either to iodination or to bromination; we therefore consider the following reaction mechanism to be more probable: After loss of halogen, radicals containing trivalent carbon are formed; these can either directly add on to one another or react with fresh molecules of the halogenated derivative. The resultant new radicals add on to the molecule of dihalo-substituted ester, and the latter readily loses halogen with formation of a double bond:



$$2CH_3COCHICOOC_2H_5 + NaI \rightarrow 2CH_3CO\underset{|}{C}HCOOC_2H_5 + NaI_3;$$

$$CH_3CO\underset{|}{C}HCOOC_2H_5 + CH_3COCHICOOC_2H_5 \rightarrow CH_3COCH_2COOC_2H_5 + CH_3COCI\underset{|}{C}OOC_2H_5;$$

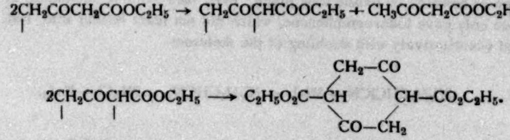
$$2CH_3COC\underset{|}{I}COOC_2H_5 \rightarrow \begin{array}{c} CH_3COCICOOC_2H_5 \\ | \\ CH_3COCICOOC_2H_5; \end{array}$$

$$\begin{array}{c} CH_3COCICOOC_2H_5 \\ | \\ CH_3COCICOOC_2H_5 \end{array} + NaI \rightarrow \begin{array}{c} CH_3COCCOOC_2H_5 \\ \| \\ C_2H_5OOCCCOCH_3 \end{array} + NaI_3.$$

Finally, with chloro- and bromo- derivatives a reaction of the radical $CH_3CO\underset{|}{C}HCOOC_2H_5$ with these compounds is possible with subsequent replacement of chlorine or bromine by iodine even in the doubled molecule.

For verification of the hypothesis, we carried out a detailed investigation of the products of reaction with α-bromoacetoacetic ester, and isolated and identified halogen-free acetoacetic ester. Its yield was nearly theoretical.

The reaction of γ-bromoacetoacetic ester with sodium iodide was even more complicated, succinylsuccinic ester being formed. It is possible that reaction between the radical formed $-CH_2COCH_2COOC_2H_5$ and another such radical takes place with removal of the more active hydrogen of the middle CH_2 group:



$$2\underset{|}{C}H_2COCH_2COOC_2H_5 \rightarrow \underset{|}{C}H_2CO\underset{|}{C}HCOOC_2H_5 + CH_3COCH_2COOC_2H_5.$$

The marked difference in the behavior of halogenated derivatives of malonic ester, acetoacetic ester and analogs on the one hand, and benzyl halides or halogenated acetophenones (containing not less active halogen atoms) on the other hand, is explained by the difference in types of reactivity of the halogen. The latter may split off from a carbon either in the form of an anion or in the form of a neutral atom. This is clearly demonstrated, for example, by experiments with labeled atoms [3]. Iodide salts act with the iodine anion, which in forming the complex anions I'_3, I'_5, etc. can add on only neutral atoms or the I_2 molecule but never other such anions. Hence the doubling of the skeleton of a molecule on reaction with iodides can proceed only with halogen derivatives with an atom-radical type of reactivity. Consequently, after we have determined the particular character of the reactivity of a halogenated organic compound, we can then with high probability predict whether the method here under consideration for increasing the complexity of a carbon skeleton is applicable to a given compound.

EXPERIMENTAL

Preparation of halogenated derivatives. A number of halogenated derivatives were available without preparation. Bromobenzyl cyanide was obtained by bromination of benzyl cyanide. Chlorobenzyl cyanide was prepared by the action of thionyl chloride on mandelonitrile. The ethyl esters of phenylchloroacetic and phenylbromoacetic acids were prepared from the acid halides of the halogen derivatives of phenylacetic acid and alcohol. Phenyliodoacetic ester was prepared from phenylbromoacetic ester and sodium iodide. A dark oil was obtained which decomposed when distilled in vacuum. Analysis without distillation gave 39.7% iodine (the theoretical amount is 43.8%). This substance had to be used in experiments without purification. α-Chloroacetoacetic ester was prepared by adding sulfuryl chloride to acetoacetic ester cooled to 0°. α-Bromoacetoacetic ester was prepared by the action of bromine in carbon disulfide on copper-acetoacetic ester. γ-Bromoacetoacetic ester was prepared by the action of a mixture of bromine and CS_2 on a carbon disulfide solution of acetoacetic ester. α-Iodoacetoacetic ester was obtained by the action of an ethereal solution of iodine upon copper-acetoacetic ester.

Experimental procedure. We adopted the procedure of [1], i.e. we performed the reaction in acetone solution. In some cases methyl ethyl ketone (with a higher boiling point) was used as solvent. To a solution of sodium iodide was added the organic halogen compound. The mixture was refluxed on a water bath, then cooled, decolorized with sodium thiosulfate and diluted with water. The separated product was purified by recrystallization from alcohol, ligroine or another solvent. The liquid products were purified by vacuum distillation.

Results of experiments. 1. 3 g $C_6H_5CHClCO_2C_2H_5$, 3.4 g NaI and 20 ml acetone were heated 4 ½ hours. 1 g of product was obtained. This melted at 136° after crystallization from alcohol. The literature reports m.p. 136° and 140° [4] for the ester of diphenylsuccinic acid. After heating with KOH, diphenylsuccinic acid with m.p. 228-230° [5] was isolated.

2. 3 g $C_6H_5CHClCO_2C_2H_5$, 3.4 g NaI and 30 ml methyl ethyl ketone were heated 2 ½ hours. 0.9 g diphenylsuccinic ester was obtained with m.p. 140°; after saponification it gave an acid with m.p. 228-230°.

3. 3 g $C_6H_5CHBrCO_2C_2H_5$, 2.8 g NaI and 20 ml acetone were heated 4 ½ hours. 0.9 g diphenylsuccinic ester was isolated.

4. 3 g $C_6H_5CHBrCO_2C_2H_5$, 2.8 g NaI and 25 ml methyl ethyl ketone were heated 2 ½ hours and yielded 0.85 g diphenylsuccinic ester.

5. 7 g $C_6H_5CHICO_2C_2H_5$, 1.8 g NaI and 25 ml acetone were heated 4 ½ hours and yielded 0.9 g diphenylsuccinic ester.

6. 2 g $C_6H_5CHBrCN$, 2.3 g NaI and 20 ml acetone were heated 1 ½ hours. 1.15 g crystalline substance was obtained (m.p. 224° after crystallization from glacial acetic acid). According to the literature [6], the mixture of isomers of diphenylsuccinonitrile has m.p. 224°. Heating in a sealed tube with concentrated hydrochloric acid at 150-160° for 5 hours gave a nitrogen-free product with m.p. 227°, which is the melting point of α,α'-diphenylsuccinic acid [7].

7. 2 g $C_6H_5CHClCN$, 2.9 g NaI and 25 ml acetone were heated 1½ hours and gave 1.4 g diphenylsuccinonitrile.

8. 3 g $CH_3COCHClCO_2C_2H_5$, 4.1 g NaI and 30 ml acetone were heated 2 hours. After dilution with water, 0.6 g diacetylfumaric ester with m.p. 94° [8] was isolated.

Found %: C 56.02; H 6.47. M 255.7. $C_{12}H_{16}O_6$. Calculated %: C 56.27; H 6.25. M 256.2.

9. 3 g $CH_3COCHBrCO_2C_2H_5$, 3.2 g NaI and 25 ml acetone were heated $1^1/_2$-2 hours and gave 0.2 g diacetylfumaric ester.

10. 39.4 g $CH_3COCHBrCO_2C_2H_5$, 42 g NaI and 250 ml acetone were heated 3 hours. The acetone was driven off and 250 ml diethyl ether run in. The solution was decolorized with sodium thiosulfate and washed with water. 2 g acetoacetic ester distilled off at 6-7 mm and 50-60°. The derived semicarbazone melted at 126-129°.

11. 5 g $CH_3COCHICO_2C_2H_5$, 1.5 g NaI and 20 ml acetone were heated $1^1/_2$-2 hours and gave 0.2 g diacetylfumaric ester.

12. 5 g $CH_3COCHICO_2C_2H_5$, 1.5 g NaI and 20 ml acetone were left at room temperature for 10 days. 0.6 g diacetylfumaric ester was isolated.

13. 3 g $CH_2BrCOCH_2CO_2C_2H_5$, 3.2 g NaI and 25 ml acetone were heated $1^1/_2$-2 hours. 0.43 g succinylsuccinic ester with m.p. 127° [10] was obtained.

Found %: C 56.05; H 6.15. M 256.6. $C_{12}H_{16}O_6$. Calculated %: C 56.27; H 6.25. M 256.2.

14. 30 g $CH_2BrCOCH_2CO_2C_2H_5$, 32 g NaI and 200 ml acetone were heated 2 hours and gave 4.5 g succinylsuccinic ester and 0.4 g acetoacetic ester.

15. 5 g $o\text{-}NO_2C_6H_4CH_2Cl$, 6.6 g NaI and 45 ml acetone were heated 4 hours and gave 4 g $o\text{-}NO_2C_6H_4CH_2I$ with m.p. 74° (from alcohol).

16. 7.8 g $o\text{-}NO_2C_6H_4CH_2I$, 4.5 g NaI and 30 ml acetone were heated 8 hours and gave 6 g $o\text{-}NO_2C_6H_4CH_2I$.

17. 5 g $C_6H_5COCH_2Cl$, 8.4 g NaI and 50 ml acetone were heated 6 hours and gave 4 g $C_6H_5COCH_2I$ with m.p. 25-27°.

18. 4.7 g $C_6H_5COCH_2I$, 3 g NaI and 20 ml acetone were heated 6 hours. 3 g iodoacetophenone was obtained.

SUMMARY

1. The action of sodium iodide upon a large number of haloorganic compounds was studied. It was shown that the reaction of haloorganic compounds containing one halogen atom with sodium iodide can proceed in three directions: replacement of chlorine or bromine by iodine without further transformations, replacement of chlorine or bromine by iodine with subsequent evolution of iodine and doubling of the carbon skeleton, or doubling of the carbon skeleton with formation of a double bond or with ring closure.

2. It is suggested that doubling of the carbon skeleton under the action of iodides is preceded by formation of free radicals which can join together or enter into more complex reactions.

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Received June 14, 1955

Tomsk Polytechnic Institute

UNSATURATED CYCLIC HYDROCARBONS AND THEIR DERIVATIVES

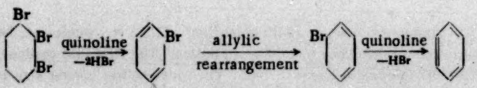
XIX. SYNTHESIS OF 1,2,3-TRIBROMOCYCLOHEXANE AND ITS REACTION WITH QUINOLINE

N. A. Domnin and M. A. Larionova

One of us earlier put forward a scheme for the mechanism of concomitant reactions of halogenation and dehalogenation [1]. To a certain degree this scheme was hypothetical but it was fruitful in the sense that it suggested a new experiment.

In a number of our investigations on concomitant reactions of halogenation and dehalogenation, unsaturated hydrocarbons of the cyclohexane series and its homologs were found to have a very marked tendency to change into benzene and its derivatives [2]. With the aim of establishing to what extent our scheme was correct, we instituted a special experiment. On the basis of our scheme we reached the conclusion that reaction of 1, 2, 3-tribromocyclohexane (first synthesized by us) with quinoline should lead to bromobenzene. However, instead of this one could expect the formation of benzene if it is assumed that the formation of the aromatic nucleus under all the conditions possible for this proceeds preferentially also by the simplest and shortest route. This was actually found to be the case. According to our scheme, the formation of bromobenzene can be accounted for only by a whole series of steps: splitting out of two molecules of hydrobromic acid, formation of quinoline perbromate, bromination of the dienic monobromide and then fresh cleavage of two molecules of hydrobromic acid [1].

In contrast to the foregoing, the formation of benzene can take place in one step – splitting out of three molecules of hydrobromic acid with allylic rearrangement of the intermediate dienic monobromide:



Consequently, our new observation particularly convincingly confirms the tendency to transformation, not only of unsaturated but also of saturated derivatives of cyclohexane substituted in the aromatic ring.

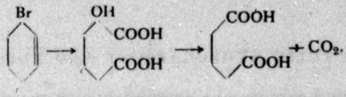
EXPERIMENTAL

Synthesis of 3-bromocyclohexene-1. 31 g 3-bromo-5, 5-dimethylhydantoin in 110 ml carbon tetrachloride was refluxed on a water bath for 20 minutes. The resultant suspension was added portionwise to 61.5 g cyclohexene. The reaction was conducted in boiling carbon tetrachloride. After cooling of the reaction mixture, the precipitate of 5,5-dimethylhydantoin was separated and washed with carbon tetrachloride. The excess of cyclohexene and carbon tetrachloride was driven off from the filtrate in vacuum at 17-20 mm.

The residue was fractionated in vacuum; a fraction coming over at 57.5-58° (12 mm) was collected; weight 14 g (60%).

B.p. 57.5-58° (12 mm), d_4^{20} 1.3998, n_D^{20} 1.5271, MR_D 35.34; calc 35.00.
Found %: Br 49.20, 49.32. C_6H_9Br. Calculated %: Br 49.62.

Proof of the structure of 3-bromocyclohexene-1 was obtained by oxidation. 2.5 g 3-bromocyclohexene-1 was oxidized with 8.5 g permanganate in a flask with a ground-glass stopper and cooled with iced water. The oxidation products were extracted by the method previously described [3]. The crystalline substance melted at 96° after recrystallization from alcohol, and a mixed melting test with an authentic sample of glutaric acid did not give a depression. It can therefore be assumed that 3-bromocyclohexene-1 oxidizes according to the scheme:



The anticipated α-hydroxyadipic acid was not detected in the products of oxidation; it was therefore oxidized further to glutaric acid, and this accounts for the larger quantity of permanganate consumed in the oxidation.

Splitting-off of hydrobromic acid from 3-bromocyclohexene-1 was effected with quinoline. 4.6 g 3-bromocyclohexene-1 and 11.6 g freshly distilled quinoline were placed in a Wurtz flask. The flask was gradually heated on Wood's metal to 140-150° and towards the end to 170-180°. The receiver was cooled with ice and salt. The distillate was washed with dilute sulfuric acid and then with water, dried over calcium chloride, and fractionated. About 1 g substance was collected at 79-80° and was identified as cyclohexadiene-1,3.

d_4^{20} 0.8410, n_D^{20} 1.4748, MR_D 26.77. C_6H_8. Calc. 26.81.

The cyclohexadiene-1,3 was condensed with maleic anhydride. 0.8 g maleic anhydride (m.p. 53°) in 3.7 g benzene and 0.8 g of the hydrocarbon were sealed into a test tube. After 5 days, 1.62 g (91%) crystals with m.p. 147° separated out. The melting point agrees with that in the literature.

Synthesis of 1,2,3-tribromocyclohexane. To 16.1 g 3-bromocyclohexene-1 in 10 ml carbon tetrachloride was added dropwise 5.1 ml (16 g) bromine in 10 ml carbon tetrachloride with vigorous stirring and cooling (ice and salt). The bromine was quickly decolorized but at the end of the reaction the solution had acquired a pale red color and started to give off hydrobromic acid. The solvent was taken off in vacuum at room temperature and the residue fractionated in vacuum on a water bath. 29 g substance coming over at 135.5-137° (5 mm) was collected.

d_4^{20} 2.1352, n_D^{20} 1.5930, MR_D 50.91, $C_6H_9Br_3$. Calc. MR_D 51.00.
Found %: Br 74.56, 74.76. $C_6H_9Br_3$. Calculated %: Br 74.71.

Reaction of 1,2,3-tribromocyclohexane with quinoline. To 12.4 g quinoline, heated to 70-80°, was added dropwise 17 g 1,2,3-tribromocyclohexane in 12.4 g quinoline. The flask was gradually heated to 150° on Wood's metal. Towards the end the temperature rose to 180°. The receiver was cooled with ice and salt. The distillate, which came over at 50-85°, was washed with dilute sulfuric acid and with water and dried over calcium chloride. 2.3 g substance was collected.

B.p. 80.5-81°, d_4^{20} 0.8812, n_D^{20} 1.5016.

The constants of the hydrocarbon agree with those of benzene. Its structure was confirmed by measurement of its ultraviolet absorption spectrum with the Beckmann spectrophotometer. The absorption region exactly coincided with the absorption region of benzene (λ_{max} 255, 262).

By reacting 1,2,3-tribromocyclohexane with alcoholic alkali, we obtained a mixture of various monobromo compounds, but we were unable to obtain consistent results in this part of the investigation.

SUMMARY

1. 1,2,3-Tribromocyclohexane was synthesized for the first time and characterized.

2. The structure of 3-bromocyclohexene-1 was confirmed by the oxidation method.

3. It was shown that reaction of 1,2,3-tribromocyclohexane with quinoline gives benzene, the formation of which is easily explained by our proposed scheme for reactions of concomitant halogenation and dehalogenation.

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Received June 16, 1955

Leningrad State University

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*T.p. = C. B. Translation pagination.

THE LIEBERMANN NITROSO GROUP REACTION

G. Ya. Vanag and E. Ya. Lukevits

As far back as 1874 Liebermann found [1] that when phenol was heated with concentrated sulfuric acid containing nitrous acid, the liquid first turned brown, then green and finally blue. The color changed to deeper blue when the liquid was diluted with water and excess of caustic alkali added.

Many nitroso compounds also give this reaction. A small amount of nitroso compound is heated with phenol and concentrated sulfuric acid. After cooling, the mixture is poured into water and excess of caustic alkali added. A blue or violet coloration appears.

Other monohydric phenols not substituted in the para-position also give the coloration with concentrated sulfuric acid and alkali. Di- and trihydric phenols also react; for example, thymol gives a green, red and a deep blue color; α-naphthol gives a green color; β-naphthol a dark green color; pyrocatechol turns green or red; hydroquinone turns green or red; phloroglucinol gives a blood-red color, etc. [2].

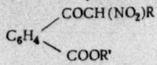
A reddish violet solution with a red fluorescence is formed when resorcinol is heated with concentrated sulfuric acid and sodium nitrite and the mixture is run into water containing excess of ammonia [3].

The Liebermann nitroso group reaction is known to be fairly "capricious" and is by no means always positive. On testing some of the dihydric phenols mentioned above in place of ordinary phenol, we found that the reaction with resorcinol goes with much greater facility. On adding a drop of dilute sodium nitrite solution to concentrated sulfuric acid containing resorcinol, a red coloration is obtained even without heating; a reddish brown fluorescence is developed when this solution is poured into water and excess of caustic alkali is added. The fluorescence disappears on acidification and reappears on addition of caustic alkali.

Since the literature contains no information about the sensitivity of this reaction, we determined the sensitivity both with phenol and with resorcinol. The limiting dilution of nitrous acid at which a blue color is still developed with phenol is 1:41,000; with resorcinol the reddish-orange fluorescence is still visible at a dilution of 1:44,000.

Since many nitroso compounds lose nitrous acid under the action of concentrated sulfuric acid, these nitroso compounds also give the above color reactions with phenol and resorcinol, for example nitrosamines and nitrosophenols. But if the nitroso group is more firmly attached, it does not split off under the reaction conditions in the form of nitrous acid. Such compounds do not give a positive reaction, examples out of many being p-nitrosodimethylaniline and ethyl p-nitrosocinnamate.

Thus the Liebermann reaction is not essentially a reaction for the nitroso group, as this is usually defined, but a reaction for nitrous acid split off from the substance under investigation under the reaction conditions.

It is to be fully expected that some nitro compounds will also split off nitrous acid under the action of sulfuric acid, and consequently they should also give a positive Liebermann reaction. This expectation was fully confirmed by experiments. The following nitro compounds give a positive reaction both with phenol and resorcinol: phenylnitromethane, ω-nitrostyrene, nitromethylenephthalide, 1-nitromethyl-1-methoxyphthalide, 2-nitro-2-phenylindanedione-1,3, phenylnitroacetophenone-o-carboxylic acid, the methyl ester of ω-nitroacetophenone-o-carboxylic acid, a whole series of compounds of the type of  $C_6H_4\begin{cases}COCH(NO_2)R\\COOR'\end{cases}$ [4], and others.

The reaction with resorcinol is performed in the following manner: A little of the substance and resorcinol are covered with concentrated sulfuric acid. The latter quickly turns red, usually without heating. A pink solution is formed when water is added. Addition of excess alkali colors the solution red to violet and a red-brown or red-orange fluorescence is developed.

SUMMARY

The Liebermann reaction is not a specific reaction for the nitroso group; it is a reaction for the nitrous acid split off from the nitroso compound under the reaction conditions. A positive reaction is also given by those nitro compounds capable of splitting off nitrous acid under the reaction conditions.

Resorcinol is a more convenient reagent than phenol for the reaction for liberated nitrous acid. The reaction with resorcinol takes place with greater facility, usually without heating, and is not less sensitive than the reaction with phenol. A red solution is formed which, after dilution with water and addition of excess of caustic alkali, is transformed into a red-violet solution, and a characteristic red-brown or red-orange fluroescence is developed.

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Received May 23, 1955

Latvian State University

CLEAVAGE OF TRI-p-TOLYLANTIMONY AND TRI-α-NAPHTHYLANTIMONY BY ACID CHLORIDES AND ALKYL HALIDES IN PRESENCE OF ALUMINUM CHLORIDE

M. S. Malinovsky and S. P. Olifirenko

In preceding communications we showed that acid chlorides in presence of anhydrous aluminum chloride cleave triphenylantimony, diphenylchloroantimony and phenyldiiodoantimony with formation of fatty-aromatic ketones [1]. Similarly to the action of acid chlorides, the above-mentioned organoantimony compounds are also cleaved by alkyl halides with formation of the corresponding fatty-aromatic hydrocarbons [1, 2]. Continuing our study of these reactions, we have investigated the cleavage of tri-p-tolylantimony and tri-α-naphthylantimony with acid chlorides and alkyl halides in presence of aluminum chloride. We considered the investigation to be of interest for the following reason: One of us had previously shown, during cleavage with acid chlorides of organoarsenic compounds, that the acyl residue of the acid chloride takes the place of the arsenic [3]. This suggested to the author the possibility of clarifying the structure of aromatic arsenic compounds, since the resultant ketones were not only closely studied but also easily identified. Evidently organoantimony compounds with aromatic radicals will be cleaved in exactly the same manner, i.e. the acyl residue of the acid chloride occupies the position of the cleaved-off antimony, and consequently the constitution of the resultant ketone should reveal the position of the antimony in the benzene ring. These considerations prompted us to undertake the present investigation. At the same time, we thought it would be expedient to consider also the mechanism of cleavage of organoantimony compounds by acid chlorides and alkyl halides in presence of aluminum chloride which can be also applied to the cleavage of other organometallic compounds (arsenic, tin, lead, etc.).

We cleaved tri-α-naphthylantimony with acetyl chloride and propionyl chloride, and also with isopropyl bromide and n-butyl bromide.

Fatty-aromatic Ketones and Hydrocarbons Obtained by Cleavage of Tri-p-tolyl- and Tri-α-naphthylantimony

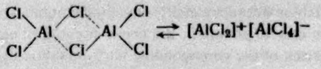
Compound cleaved	Products of reaction	Boiling point	Yield (%)	Percent of antimony cleaved
	Ketones			
p-$(CH_3C_6H_4)_3Sb$.	p-CH_3—CO—C_6H_4—CH_3	225—227°	60.71	86.66
ditto	p-C_2H_5—C_6H_4—CH_3	237—239	63.33	86.90
ditto	p-$(CH_3)_2CH$—CO—C_6H_4—CH_3	242—244	81.25	92.67
α-$(C_{10}H_7)_3Sb$ . . .	CH_3—CO—$C_{10}H_7$-α	294—298	62.59	86.13
ditto	C_2H_5—CO—$C_{10}H_7$-α	304—306	55.24	86.25
	Hydrocarbons			
p-$(CH_3C_6H_4)_3Sb$.	p-CH_3—C_6H_4—$CH(CH_3)_2$	175—177°	76.08	89.92
ditto	p-CH_3—C_6H_4—C_4H_9-n	197—199	77.77	89.85
ditto	p-CH_3—C_6H_4—C_4H_9-iso	195—197	81.11	90.50
α-$(C_{10}H_7)_3Sb$ . . .	α-$C_{10}H_7$—$CH(CH_3)_2$	259—260	58.48	86.11
ditto	α-$C_{10}H_7$—C_4H_9-n	280—284	60.08	86.46

Tri-p-tolylantimony was cleaved with acetyl chloride, propionyl chloride and isobutyryl chloride, and also with isopropyl, isobutyl and butyl bromides. Cleavage yielded the corresponding fatty-aromatic ketones or fatty-aromatic hydrocarbons which are listed in the table.

The table shows that the yields of ketones and hydrocarbons are quite high. The acyl group of the acid chloride or the radical of the alkyl halide occupies the position previously occupied by antimony in the organometallic compound. However, the amount of ketone or hydrocarbon obtained does not indicate the percent of antimony compound decomposed. As we see from the last column of the table, the percent of cleaved-off antimony is considerably higher and reaches 86 % and sometimes higher. Thus, the yield of ketone or hydrocarbon must be considerably higher than indicated, but during the reaction the yield is lowered by partial resinification.

We shall consider the mechanism of cleavage of organoantimony compounds with acid chlorides in presence of aluminum chloride with reference to triphenylantimony, taking into account the data of Gustavson [4], Korshak [5], Lebedev [6] and other investigators of reactions with aluminum chloride [7].

Aluminum chloride is known to have a dimeric molecule in the form of a dipole:



On coming into contact with $(C_6H_5)_3Sb$, aluminum chloride causes cleavage of one phenyl radical:

$$(C_6H_5)_3Sb + [AlCl_2]^+[AlCl_4]^- \rightarrow [C_6H_5]^- + [(C_6H_5)_2Sb]^+ + [AlCl_2]^+ + [AlCl_4]^-.$$

The radical $[C_6H_5]^-$ and $[AlCl_2]^+$ can form the organoaluminum compound $C_6H_5AlCl_2$. Subsequently $[AlCl_4]^-$ reacts with $[(C_6H_5)_2Sb]^+$ according to the equation:

$$[(C_6H_5)_2Sb]^+ + [AlCl_4]^- \rightarrow (C_6H_5)_2SbCl + AlCl_3.$$

During this process $(C_6H_5)_2SbCl$ was actually detected [1]. Concerning $C_6H_5AlCl_2$, its presence was established by the formation of benzene on decomposition with water of the product of reaction of triphenylantimony with aluminum chloride.

Diphenylantimony subsequently undergoes the same transformations. If an acid chloride is present in the reaction medium, it forms the complex $RCOCl \cdot AlCl_3$. This complex reacts with the intermediate organoaluminum compound $C_6H_5AlCl_2$ according to the equation:

$$C_6H_5AlCl_2 + RCOCl \cdot AlCl_3 \rightarrow C_6H_5COR \cdot AlCl_3 + AlCl_3.$$

A ketone is obtained when the new and stable complex $C_6H_5COR \cdot AlCl_3$ is treated with water.

The reaction scheme remains the same in cleavage of organoantimony compounds with alkyl halides in presence of aluminum chloride. However, the complex of alkyl halide with $AlCl_3$ is less stable than that of acid chloride with aluminum chloride. Due to this, the resultant complex $C_6H_5R \ldots AlCl_3$ is not stable and breaks down under normal conditions with loss of free $AlCl_3$:

$$C_6H_5AlCl_2 + RCl \rightarrow C_6H_5R \ldots AlCl_3,$$
$$C_6H_5R \ldots AlCl_3 \rightarrow C_6H_5R + AlCl_3.$$

The aluminum chloride is again transformed into the dimer Al_2Cl_6 which then repeats the process from the start with a fresh molecule of the stibine. Thus, during the whole period of reactions with alkyl halides the aluminum chloride is regenerated. This explains why the amount of aluminum chloride for the reaction with alkyl halides can be very much less than in the reaction with acid chlorides [2].

EXPERIMENTAL

Tri-α-naphthylantimony was prepared by the Grignard reaction from α-bromonaphthalene, magnesium and antimony trichloride [8]. It had m.p. 216-217°, in agreement with the literature.

Tri-p-tolylantimony was obtained by the Wurtz-Michaelis reaction [9]. We consider it necessary to detail this synthesis here since we did not find a description in the literature.

Antimony trichloride and p-$CH_3C_6H_4Br$ (b.p. 183-185°) were brought into reaction in equimolar amounts, and double the required amount of sodium was taken. The whole of the reaction was carried out in a medium of absolute ether to which was added a few milliliters of ethyl acetate as catalyst. Working up in the usual fashion gave an oil which distilled in vacuum at 218-222° (3 mm). It crystallized poorly. It was purified by recrystallization from acetone and then from a large volume of alcohol. Colorless crystals were obtained with m.p. 122° (after 3 recrystallizations from alcohol), which is a little lower than the melting point of the product synthesized by Grignard [8]. Yield of the stibine 70%.

We calculated the required amounts of tri-α-naphthylantimony and tri-p-tolylantimony and of acid chloride or alkyl chloride from the equations:

$$Ar_3Sb + 3ClCOR \rightarrow 3ArCOR + SbCl_3,$$
$$Ar_3Sb + 3BrR \rightarrow 3ArR + SbBr_3.$$

The following quantities were taken for each cleavage experiment: 1) tri-α-naphthylantimony 7.2 g (0.014 mole), acid chloride or alkyl halide 0.051 mole, aluminum chloride 5.71 g (0.043 mole) and carbon disulfide 100 g; 2) tri-p-tolylantimony 8 g (0.02 mole), acid chloride or alkyl halide 0.06 mole, aluminum chloride 8 g (0.06 mole) and carbon disulfide 100 g.

The cleavage experiments were carried out as described in preceding communications. The ketones or hydrocarbons obtained were purified by distillation. Determinations were made of their boiling point, specific gravity and refractive index, which usually agreed with the literature data [10]. The semicarbazone of each ketone was prepared and its melting point determined.

After decomposition of the reaction mixture with iced water, the antimony trichloride was precipitated from the aqueous solution with carbon disulfide. From the amount of trichloride precipitated, the percent of cleaved antimony was determined. The antimony content of the resinous residue after distillation of the ketone or hydrocarbon was also determined.

SUMMARY

1. Tri-α-naphthylantimony and tri-p-tolylantimony were cleaved with acid chlorides in presence of aluminum chloride with formation of the corresponding fatty-aromatic ketones in yields of up to 60-70%.

2. The same organoantimony compounds are cleaved by alkyl halides in presence of aluminum chloride with formation of the corresponding fatty-aromatic carbons in yields of up to 60-75%.

3. The method of cleavage of organoantimony compounds with acid chlorides or alkyl halides in presence of aluminum chloride can be utilized for establishment of the structure of a stibine, since the acyl group of the acid chloride or the radical of the alkyl halide enters the position of the cleaved antimony.

4. A more probable mechanism of the reactions is proposed; this assumes the formation of intermediate organoaluminum compounds and the dimeric structure of aluminum chloride. The proposed mechanism can explain the cleavage of all other organometallic compounds in presence of aluminum chloride by acid chlorides or alkyl halides.

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Received June 24, 1955

Lvov State University

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COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

XVI. REACTION OF AMMONIA WITH ESTERS OF GLYCIDIC ACIDS

V. F. Martynov, Zh. D. Vasyutina and L. P. Nikulina

Only the β-monoalkyl- or arylglycidic acids were investigated in earlier studies of the action of ammonia on glycidic acids. Glycidic acids containing two substituents in the β-position are the most accessible preparatively but have been almost completely neglected in such investigations. Abderhalden [1] attempted, but without success, to isolate the product of reaction of ammonia with the ethyl ester of β,β'-dimethylglycidic acid. We [2] repeated this experiment and were able to isolate the reaction product and to confirm its structure. Thus, of the glycidic acids containing a tertiary carbon atom in the β-position, only the ethyl ester of β,β'-dimethylglycidic acid has been studied in respect of behavior towards ammonia.

The present work is a continuation of our preceding communication [2]. We studied the ethyl esters of glycidic acids containing various substituents at the tertiary β-carbon atom, namely the ethyl esters of β-methyl-β-ethylglycidic acid (I), β-tetramethyleneglycidic acid (II), β-pentamethyleneglycidic acid (III), β-methyl-β-phenylglycidic acid (IV) and β,β' diphenylglycidic acid (V). The reaction was performed with aqueous or alcoholic solution of ammonia in sealed tubes with heating.

The reaction with ammonia goes in two stages. At first the amides of the corresponding glycidic acids are formed and these then react further with opening of the oxide ring and with formation of the amides of the hydroxyamino acids. Replacement of the ester group by the amido group proceeds with much greater facility than the opening of the oxide ring, so that the reaction can always be stopped at the stage of formation of the amide. This is particularly easily effected in glycidic acids containing large substituents in the β-position whose steric hindrances markedly lower the reactivity of the oxide ring. In practice the amides are easily formed at room temperature if the mixture of substances is left for 24 hours. It should be noted that the formation, not of amides but of ammonium salts of the glycidic acids, is sometimes observed when working with aqueous solutions of ammonia with application of heat.

Opening of the oxide ring of glycidic acids, as our investigations showed, varies markedly with change of substituents at the β-carbon atom. The most reactive were the amides of β-tetramethylene and β-methyl-β-ethylglycidic acids. The amide of β-tetramethyleneglycidic acid reacts with particular facility and the reaction can go at room temperature. Exceptional reactivity of the oxide ring of this glycidic acid was also noted by us earlier in the reaction with aniline [3]. We explain this on the basis of the five-membered ring being planar, substituents in the β-position being repelled to the maximum extent from the oxide ring. On transition to the amide of β-pentamethyleneglycidic acid, the reactivity is sharply diminished. The oxide ring is greatly stabilized.

Whereas the amide of β-tetramethyleneglycidic acid reacted with ammonia with opening of the oxide ring in the course of 6 hours on heating to 100° or at the ordinary temperature in the course of several days, these conditions proved too mild for the amide of β-pentamethyleneglycidic acid. Heating of the ethyl ester of β-pentamethyleneglycidic acid with ammonia to 100° for 6 and for 20 hours led only to formation of the amide, which could be isolated by simple shaking of an aqueous solution of ammonia with the glycidic ester at room temperature. Rise of temperature to 130-140° is necessary to enable the reaction to proceed as far as opening of the oxide ring with formation of the corresponding amide of the hydroxyamino acid. Stabilization of the oxide ring is evidently caused by an increase in steric hindrance on passing from the planar five-membered ring to the bent six-membered ring.

Similar observations of change of reactivity were made on transition from the amide of β-methyl-β-ethylglycidic acid to the amide of β-methyl-β-phenylglycidic acid. Whereas the former reacts with aqueous ammonia solution with opening of the ring in the course of 6 hours on heating to 100°, the latter for the same period in alcoholic ammonia solution (which acts more vigorously) only gives the amide of β-methyl-β-phenylglycidic acid. Increase of the period of heating to 9 hours led, judging by the analyses, to a mixture of amide and addition product, and only after heating for 20 hours was the pure addition product – the amide of β-phenylhydroxy aminobutyric acid – obtained. It was natural to expect after this that on transition from the amide of β-methyl-β-phenylglycidic acid to the amide of β,β'-diphenylglycidic acid a fresh lowering of the activity of the oxide ring would be observed.

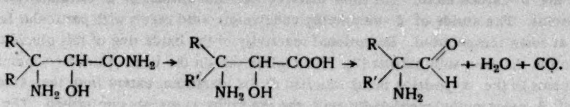
Actually, heating with alcoholic ammonia solution at 100° for 6 and then for 24 hours did not lead to the desired result. In both cases only the amide of β,β'-diphenylglycidic acid was obtained. And only after carrying out the reaction at 130° for 16 hours was opening of the oxide ring finally effected with formation of the amide of β,β'-diphenylhydroxyaminopropionic acid. Consequently, the evaluation up to now of the reactivity of the oxide ring enables the investigated esters of glycidic acids to be arranged in the following order of reactivity: (II) > (I) > (IV) > (III) > (V).

It should be noted that the relative positions of the last two members of this series is not as definite as that of the first three members.

As was already pointed out, the reaction of glycidic esters with ammonia gives two types of products – amides of glycidic acids and amides of hydroxyamino acids. Amides of glycidic acids are obtained as a rule in the form of crystalline compounds whose isolation and purification do not cause difficulties.

Amides of hydroxyamino acids, however, are obtained in the form of resinous masses which cannot be purified by the usual methods. Only in the case of β-methyl-β-phenylglycidic ester did we succeed in isolating the corresponding amide of the hydroxyamino acid in the crystalline state. This is probably because the oxide ring reacts not only with ammonia to form the hydroxyamino acid, but also with water which is always present in sufficient amount even when the reaction is carried out with alcoholic ammonia. In the latter case amides of substituted glycerinic acids should be formed. In a series of papers [4,5] P. Melikov actually showed that glycidic acids add on the elements of water with extremely great facility when heated and form syrupy substituted glycerinic acids; therefore, we separated the products of addition of ammonia – amides of hydroxyamino acids – in the form of their hydrochlorides. The yield of reaction products at the best did not exceed 60%, which is further evidence that side reactions take place. The formulas of the products that we obtained are given below.

Evidence of the structure of the hydroxyamino acids was obtained by our previously applied method [6], which is based on the observation that α-hydroxy-β-amino acids evolve the elements of formic acid under the action of concentrated sulfuric acid and are transformed into α-aminoaldehydes. Thus, in the present case the oxide ring of glycidic acids under the action of ammonia is opened from the side of the β-carbon atom with formation of α-hydroxy-β-amino acids, and under the action of sulfuric acid the corresponding α-aminoaldehydes should be obtained, while the formic acid should break down to water and carbon monoxide:



In fact, all the addition products broke down under the action of sulfuric acid with copious evolution of bubbles of gas which, as shown in our preceding communications [7], could only be carbon monoxide.

The temperature of breakdown of the α-hydroxy-β-amino acids did not remain constant but fell with substitution of aromatic for aliphatic radicals in the β-position. Thus, amides of α-hydroxy-β-amino acids with aliphatic radicals broke down at 160-170°; those with one aromatic radical decomposed at 140-150°, and those with two aromatic radicals at 120-125°.

Although mere observation of the reaction course gave evidence of the presence of α-hydroxy-β-amino acids, it was necessary to isolate the corresponding aminoaldehydes or their derivatives in order to obtain final

TABLE 1

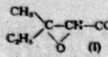
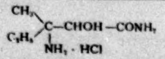
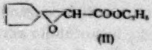
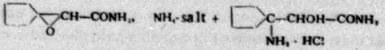
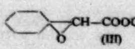
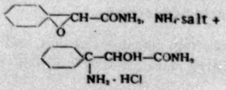
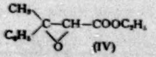
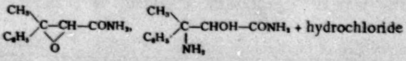
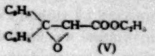
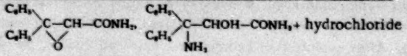
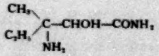
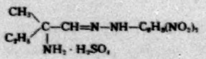
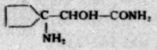
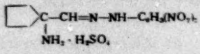
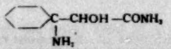
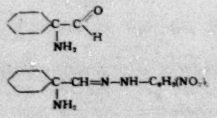
Starting substances	Products of reaction
 (I)	
 (II)	
 (III)	
 (IV)	
 (V)	

TABLE 2

Starting substances	Products of reaction
	
	
	

confirmation of this hypothesis. We were able to isolate these for three amides of α-hydroxy-β-amino acids containing aliphatic radicals in the β-position. Thus, from the amide of α-hydroxy-β-amino-β-pentamethylenepropionic acid we obtained α-aminohexahydrobenzaldehyde in the form of colorless crystals; its derivative with 2,4-dinitrophenylhydrazine was also prepared. The free aldehydes could not be isolated in the case of two other amides of α-hydroxy-β-amino acids, and only their 2,4-dinitrophenylhydrazones were obtained in the form of the sulfates.

Formulas of starting substances and of the aminoaldehydes obtained are given above.

We were unable to isolate the corresponding aminoaldehydes in the case of amides of α-hydroxy-β-amino acids containing aromatic radicals, and in this case we could not conclusively claim to have actually obtained the α-hydroxy-β-amino acids. However, no examples are yet known of ammonia combining with glycidic acids to form α-amino-β-hydroxy acids. As shown by our own investigations on β,β'-dialkyl-substituted glycidic acids and the investigations of Fourneau and Billeter [8] on β-phenylglycidic acid, ammonia adds on in both cases at the β-position.

In the case of diphenylglycidic acid it must be mentioned that the linkage of the oxygen in the oxide ring with the β-carbon atom is unstable, and this is reflected in the fact that it isomerizes to the keto acid more easily than any other of the hitherto known glycidic acids. It is therefore highly probable that the oxide ring is opened from the side of the β-carbon atom under the action of ammonia.

EXPERIMENTAL

Reaction of ethyl β-methyl-β-ethylglycidate with ammonia. 20 g of the ester in admixture with 100 ml concentrated aqueous ammonia solution (30%) were heated in a sealed glass tube for 6 hours at 100°.

After the tube had been opened, the excess ammonia and water were driven off in vacuum. The residue – a brown vitreous mass – was dissolved in anhydrous alochol and a stream of dry hydrochloric acid was passed through the solution; after a week, a precipitate of the hydrochloride of the amide of α-hydroxy-β-amino-β-methyl-β-ethylpropionic acid had formed.

After recrystallization from anhydrous alcohol and washing of the precipitate with ether, 5 g (20%) pure product was obtained. Melting point 198-200° (with decomposition).

Found %: N 15.42. $C_6H_{15}O_2N_2Cl$. Calculated %: N 15.34.

Decomposition of the hydrochloride of the amide of α-hydroxy-β-amino-β-methyl-β-ethylglycidic acid. To 1 g of the hydrochloride of α-hydroxy-β-amino-β-methyl-β-ethylpropionic acid, in a round-bottomed flask, was added 7 ml concentrated sulfuric acid. The addition was accompanied by violent evolution of hydrochloric acid. After evolution of hydrochloric acid had ceased, the reaction mixture was heated over a bare flame while stirring. Bubbles of carbon monoxide started to come off at 150°. Heating was conducted at 160-170° until only little gas was coming off. The darkened solution was poured into iced water and neutralized with caustic alkali; the aminoaldehyde was distilled off with steam. A solution of 2,4-dinitrophenylhydrazine was added to the distillate; yellowish orange needles of the sulfate of the 2,4-dinitrophenylhydrazone of aminomethylethylacetaldehyde came down. M.p. 215-216° (with decomposition).

Found %: N 18.64. $C_{11}H_{17}O_8N_5S$. Calculated %: N 18.47.

Preparation of the amide of β,β'-tetramethyleneglycidic acid. A mixture of 40 g ethyl β-tetramethyleneglycidate and 150 ml 30% aqueous ammonia was shaken in a thick-walled bottle tightly closed with a rubber stopper. The mixture was left overnight. The next day the bottle contained white acicular, silky crystals of the amide of β-tetramethyleneglycidic acid. Weight 26.7 g. From the filtrate was isolated a further 2.5 g amide. Total yield 88%. After recrystallization from benzene the m.p. was 144-145°.

Found %: N 10.10. $C_7H_{11}O_2N$. Calculated %: N 9.93.

Reaction of ethyl ester of β-tetramethyleneglycidic acid with ammonia in an aqueous medium. 10 g of ethyl tetramethyleneglycidate and 50 ml 30% aqueous ammonia were heated in a sealed ampoule at 100° for 6 hours, after which the water and excess ammonia were driven off in vacuum.

The residue contained a brown resin. This was dissolved in anhydrous ethyl alcohol, and the solution deposited the white ammonium salt of tetramethyleneglycidic acid. The precipitate was filtered and recrystallized from 40-50% ethyl alcohol. M.p. 222-223° (with decomposition). Yield 0.8 g (8.5%).

Found %: N 8.9. $C_7H_{13}O_3N$. Calculated %: N 8.8.

Dry hydrochloric acid gas was passed into the filtrate for an hour with cooling with iced water. The white precipitate of the hydrochloride of the amide of α-hydroxy-β-aminotetramethylenepropionic acid was filtered. Yield 4.8 g (42%).

The compound melted at 217-218° (with decomposition) after recrystallization from anhydrous ethyl alcohol.

Found %: N 14.60. $C_7H_{15}O_2N_2Cl$. Calculated %: N 14.40.

Reaction of ethyl β-tetramethyleneglycidate with ammonia in a medium of anhydrous alcohol. An alcoholic solution of ammonia was used for the reaction: anhydrous alcohol was saturated at 0° for 4-5 hours with gaseous ammonia which was first passed through a drying tube containing solid caustic alkali.

10 g ethyl β-tetramethyleneglycidate was heated in a sealed tube at 100° for 6 hours with 50 ml alcoholic ammonia solution.

The resinous material remaining after removal in vacuum of the alcohol and excess ammonia was dissolved in anhydrous ethyl alcohol, and a stream of dry hydrochloric acid was passed into the solution for an hour. The white hydrochloride of the amide of α-hydroxy-β-amino-β-tetramethylenepropionic acid came down. Yield 6.4 g (56%).

Found %: N 14.32. $C_7H_{15}O_2N_2Cl$. Calculated %: N 14.40.

Decomposition of the hydrochloride of the amide of α-hydroxy-β-aminotetramethylenepropionic acid with concentrated sulfuric acid. 13 ml concentrated sulfuric acid was added to 2 g substance. Hydrochloric acid was given off. The mixture was heated with stirring over a bare flame. Bubbles of carbon monoxide came off at 140-150°. After gas evolution had ceased, the hot, dark-colored liquid was poured on to ice, neutralized with caustic alkali and distilled with steam. Reaction of the transparent distillate with 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone in a yield of 0.7 g (29.3%). The precipitate was recrystallized from 40-50% ethyl alcohol. M.p. 207-208° (with decomposition).

Found %: N 18.5. $C_{12}H_{17}O_8N_5S$. Calculated %: N 17.9.

Preparation of the amide of β-pentamethyleneglycidic acid. 16 g ethyl β-pentamethyleneglycidate and 80 ml 30% aqueous ammonia were shaken in a thick-walled bottle. After standing for 3 days, white crystals of amide of β-pentamethyleneglycidic acid came down. Yield 8.1 g (60%). The m.p. was 137-138° after two recrystallizations from benzene; the literature gives 139° [9].

Found %: N 9.37. $C_8H_{13}O_2N$. Calculated %: N 9.03.

Reaction of ethyl β-pentamethyleneglycidate with ammonia in an aqueous medium. 10 g ethyl β-pentamethyleneglycidate and 50 ml 30% aqueous ammonia were heated in a sealed tube for 6 hours at 100°. The tube was opened and the contents evaporated in vacuum to leave crystals of the ammonium salt of β-pentamethyleneglycidic acid. Weight 5.1 g (54%). Readily soluble in water, insoluble in ethyl alcohol. M.p. 253-254° (with decomposition) after recrystallization from 30% alcohol.

Found %: N 8.14. $C_8H_{15}O_3N$. Calculated %: N 8.09.

Reaction of the ethyl ester of β-pentamethyleneglycidic acid with ammonia in a medium of anhydrous alcohol. 10 g ethyl β-pentamethyleneglycidate and 50 ml alcoholic ammonia solution, saturated at 0°, were heated in a sealed ampoule for 10 hours at 130-140°. After completion of the heating the ethyl alcohol and the excess ammonia were distilled off from the reaction mixture in vacuum. A brownish resinous mass remained in the distillation flask and did not crystallize on standing. The resinous product was dissolved in anhydrous ethyl alcohol and a stream of dry hydrochloric acid was passed into the solution for 3 hours while cooling with iced water.

After standing overnight the hydrochloride of the amide of α-hydroxy-β-amino-β-pentamethylenepropionic acid came down. Yield 5 g (44%).

The crystals dissolve readily in water and are insoluble in ethyl alcohol. M.p. 233-234° (with decomposition) after recrystallization from 50% ethyl alcohol.

Found %: N 13.29. $C_8H_{17}O_2N_2Cl$. Calculated %: N 13.43.

Decomposition of the hydrochloride of the amide of α-hydroxy-β-amino-β-pentamethylenepropionic acid with concentrated sulfuric acid. To 5 g of the substance was added 30 ml concentrated sulfuric acid;

hydrochloric acid came off. The mixture was heated over a naked flame with stirring (thermometer in liquid). During the heating the hydrochloride dissolved. Evolution of gas bubbles (carbon monoxide) was observed at 160-170° and the liquid darkened. After $1\frac{1}{2}$ hours, when gas evolution had slowed down, the hot dark liquid was poured on to ice and the acid neutralized with sodium hydroxide solution (until the reaction was alkaline); the mixture was then distilled with steam. White crystals of α-aminohexahydrobenzaldhyde came over with the water. Yield 0.4 g (13%). M.p. 81-82° after two recrystallizations from ligroine.

Found %: N 11.43. M 123 (by Rast's method). $C_7H_{13}ON$. Calculated %: N 11.02. M 127.

The liquid which came over with the steam and was filtered from the crystals gave a silver mirror reaction. With 2,4-dinitrophenylhydrazine it gave a yellow precipitate of hydrazone which was twice recrystallized from 30-40% aqueous alcohol. M.p. 137-138°. The same hydrazone was obtained from the crystals.

Found %: N 22.08. $C_{13}H_{17}O_4N_5$. Calculated %: N 22.8.

Reaction of ethyl β-methyl-β-phenylglycidate with ammonia in a medium of anhydrous alcohol. 10 g of the ester and 50 ml concentrated (30%) alcoholic ammonia were heated in a sealed ampoule at 100° for 6 hours. After removal in vacuum of the excess ammonia and the alcohol, the flask contained a resinous yellow-brown mass which was dissolved in a small quantity of anhydrous alcohol. The following day, crystals of the amide of β-methyl-β-phenylglycidic acid came down. M.p. 157-158° after two crystallizations from absolute alcohol. Yield 2.5 g (29%).

Found %: N 8.09. $C_{10}H_{11}O_2N$. Calculated %: N 7.91.

10 g of ethyl β-methyl-β-phenylglycidate and 50 ml concentrated (30%) alcoholic ammonia were heated in a sealed ampoule at 100° for 20 hours. After removal of the ammonia and alcohol in vacuum, the flask contained a brown resinous mass which was dissolved in absolute alcohol. The next day a white crystalline precipitate of the amide of α-hydroxy β-amino-β-methyl-β-phenylpropionic acid came down. M.p. 148° (from absolute alcohol). Yield 2.5 g (27%).

Found %: N 14.38. $C_{10}H_{14}O_2N_2$. Calculated %: N 14.43.

A stream of dry hydrochloric acid was passed into the alcoholic filtrate. After a few days a white crystalline precipitate of the hydrochloride of the amide of α-hydroxy-β-amino-β-phenylpropionic acid came down. M.p. 223-226° (with decomposition).

Reaction of ethyl β,β'-diphenylglycidate with ammonia in a medium of absolute alcohol. 10 g of the ester and 50 ml concentrated alcoholic ammonia were heated in a sealed ampoule at 100° for 6 hours. After two days a white crystalline precipitate of the amide of β,β'-diphenylglycidic acid came out of solution. M.p. 126-127° after recrystallization from absolute alcohol.

Found % : N 6.01. $C_{15}H_{13}O_2N$. Calculated %: N 6.36.

10 g of ethyl β,β'-diphenylglycidate and 50 ml concentrated alcoholic ammonia were heated in a sealed ampoule in an autoclave with counterpressure at 130° for 16 hours. After the alcohol and ammonia had been driven off in vacuum, a resinous brown mass remained which was dissolved in anhydrous ethyl alcohol. A stream of dry hydrochloric acid was passed into the solution. The next day the entire mass crystallized. Recrystallization from a mixture of alcohol and water gave a white crystalline precipitate with m.p. 230-232° (with decomposition). Yield 4.24 g (38.6%) hydrochloride of the amide of α-hydroxy-β-amino-β,β'-diphenylpropionic acid.

Found %: N 9.57. $C_{15}H_{17}O_2N_2Cl$. Calculated %: N 9.57.

Preparation of the amide of α-hydroxy β-amino-β,β'-diphenylpropionic acid. The hydrochloride was treated with 10% sodium hydroxide solution and the acid amide was obtained in the form of a white powder with m.p. 122-123°.

Found %: N 10.97. $C_{15}H_{16}O_2N_2$. Calculated %: N 10.93.

SUMMARY

1. The reaction of ammonia with five ethyl esters of glycidic acids was studied: β-methyl-β-ethylglycidic, β-tetramethyleneglycidic, β-pentamethyleneglycidic, β-methyl-β-phenylglycidic, and β,β'-diphenylglycidic acids.

It was established that the opening of the oxide ring of the first three esters occurs from the side of the β-carbon atom. Five amides of hydroxyamino acids, not described in the literature, were prepared and characterized.

2. It was established that the reactivity of the oxide ring of glycidic acids depends in great measure upon the size of the substituents at the β-carbon atom, the activity decreasing with increasing size of substituents.

3. It was shown that under the action of concentrated sulfuric acid the amides of glycidic acids containing aliphatic radicals in the β-position are decomposed to form α-aminoaldehydes. α-Aminohexahydrobenzaldehyde, not described in the literature, was prepared and characterized.

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Received June 22, 1955

Leningrad State University

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HALOGENATION OF AROMATIC SILANES

II. PREPARATION AND PROPERTIES OF CHLORO DERIVATIVES OF DIPHENYLDICHLOROSILANE

A. Ya. Yakubovich and G. V. Motsarev

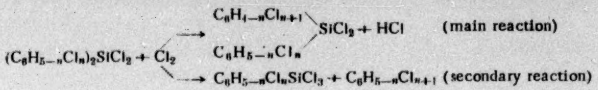
In the preceding communication [1] we described the preparation and properties of chloro derivatives of phenyltrichlorosilane. It seemed of interest to establish what influence might be exerted upon the results of chlorination by increase of the number of phenyl groups in the silane molecule linked to the silicon atom. Only one paper is known which deals with the chlorination of a silicon compound containing two phenyl groups – diphenyldichlorosilane [2]. In the latter it is reported that treatment with chlorine of diphenyldichlorosilane in presence of $FeCl_3$, $SbCl_3$ and $SbCl_5$ as catalysts at 70-120° gave chlorodiphenyldichlorosilanes containing from 6 to 10 chlorine atoms in the phenyl nuclei. Since, however, the chemical aspect of the problem and the physicochemical properties of the chloro derivatives obtained are not touched upon in the cited paper, we have undertaken a detailed study of the chlorination of diphenyldichlorosilane.

Chlorination of diphenyldichlorosilane was carried out in presence of the usual catalysts employed in halogenation of aromatic compounds (metallic iron, $AlCl_3$, $SbCl_3$, iodine, and PCl_5) [3,4]. The investigations of these reactions (in a medium of carbon tetrachloride and in its absence) in presence of Fe, $AlCl_3$ and $SbCl_3$, at temperatures of 25-85° and with various molar ratios of diphenyldichlorosilane to chlorine, led to various chlorinated diphenyldichlorosilanes ranging from monochloro- to hexachlorodiphenyldichlorosilanes in yields of 25-75%.

Chlorination of diphenyldichlorosilane in presence of iodine proceeds with very much less intensity, and even with a large excess of chlorine and at a high temperature (125°) it leads to formation as main product of only the monochloro derivative. PCl_5 is an even less active catalyst for chlorination. In the absence of catalysts diphenyldichlorosilane is not chlorinated even at 170-180° when treated for a long period with excess of chlorine.

Study of the chlorination of diphenyldichlorosilane showed that in this case the secondary process of destructive chlorination, which proceeds side by side with substitutive chlorination and is bound up with cleavage of the reacting molecules at the C–Si bonds, is more pronounced than in the chlorination of phenyltrichlorosilane under the same conditions. Thus, whereas in the chlorination of phenyltrichlorosilane this reaction is only observed to an appreciable degree when using $AlCl_3$ as catalyst, in the case of diphenyldichlorosilane the process of destructive chlorination proceeds easily, not only in presence of $AlCl_3$ but also of $FeCl_3$ and $SbCl_3$. The secondary process can be suppressed to a considerable extent by chlorinating diphenyldichlorosilane in presence of iron under mild conditions (25-30°, in a CCl_4 medium), and in turn the yield of chloro derivatives of diphenyldichlorosilane can be increased. Rise of temperature during chlorination leads to preferential rise of the velocity of the cleavage process.

The products of cleavage of diphenyldichlorosilane during its chlorination in presence of $FeCl_3$ are, on the one hand, phenyltrichlorosilane or its chloro derivatives, and, on the other hand, chloro derivatives of benzene. Thus the chlorination of diphenyldichlorosilane proceeds according to the scheme:



$$(C_6H_{5-n}Cl_n)_2SiCl_2 + Cl_2 \rightarrow \begin{matrix} C_6H_{4-n}Cl_{n+1} \\ C_6H_{5-n}Cl_n \end{matrix} \Big\rangle SiCl_2 + HCl \quad \text{(main reaction)}$$

$$(C_6H_{5-n}Cl_n)_2SiCl_2 + Cl_2 \rightarrow C_6H_{5-n}Cl_nSiCl_3 + C_6H_{5-n}Cl_{n+1} \quad \text{(secondary reaction)}$$

Chlorination of diphenyldichlorosilane in presence of $AlCl_3$ is accompanied, even under normal temperature conditions (25-30°), by the appearance of $SiCl_4$ among the reaction products; this indicates a more far-reaching side reaction than in the chlorination in presence of iron. Of the three catalysts – $AlCl_3$, $FeCl_3$ and $SbCl_3$ – the least cleavage is caused by $SbCl_3$. It was established that with this catalyst, in contrast to iron and $AlCl_3$, it is possible in the chlorination of diphenyldichlorosilane to obtain satisfactory yields of products of far-reaching chlorination containing up to 6 chlorine atoms per mole of diphenyldichlorosilane. The preparation of chlorodiphenyldichlorosilanes with a higher degree of substitution was not investigated.

The chlorination of diphenyldichlorosilane in presence of iodine is not accompanied by cleavage of the reaction products at the C–Si bond.

The influence of the catalysts, of the ratios of reactants and of the temperature upon the results of chlorination of diphenyldichlorosilane is illustrated by the data set forth in the table.

Influence of Catalysts, Ratio of Components and Temperature on the Process of Chlorination of Diphenyldichlorosilane

Conditions of chlorination of diphenyldichlorosilane						Composition of reaction products			
							chlorination products		
Experiment No.	catalyst	amount of catalyst (in % of weight of silane taken)	temperature	$(C_6H_5)_2SiCl_2/Cl_2$ molar ratio	chlorination medium	unchanged silane (%)	total yield (in %)	main product of reaction	silane cleaved (%)
1	Fe	0.5	75-80°	1:1.40	–	–	23.5	Mono-	71.0
2	Fe	0.5	28-30	1:1.45	–	–	50.0	Mono-	–
3	Fe	0.5	28-30	1:1.50	CCl_4	–	72.0	Mono-	27.5
4	Fe	0.5	30-32	1:2.30	–	–	40.0	Di-	–
5	Fe	0.5	30-32	1:2.40	CCl_4	–	68.0	Di-	31.0
6*	$AlCl_3$	0.5	25-30	1:8.40	–	–	28.0	Tetra-	70.0
7	$SbCl_3$	0.2	35-40	1:1.10	–	–	72.7	Mono-	26.0
8	$SbCl_3$	0.2	35-40	1:2.30	–	–	76.2	Di-	23.0
9	$SbCl_3$	0.3	50-55	1:3.70	–	–	60.5	Tri-, tetra-	38.0
10	$SbCl_3$	0.3	55-75	1:5.50	–	–	59.5	Tetra-, penta-	40.0
11	$SbCl_3$	0.4	50-85	1:7.00	–	–	54.0	Penta-, hexa-	44.0
12	Iodine	1.0	35-40	1:2.40	–	18.0	70.8	Mono-	–
13	Iodine	1.0	100-125	1:5.75	–	–	73.7	Mono-	–
14	PCl_5	1.0	100-140	1:5.75	–	65.0	18.0	Mono-	–

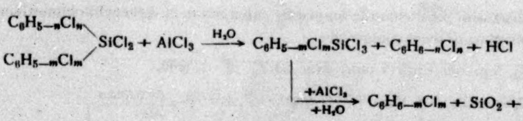
Note. Experiment performed with the objective of determining maximum degree of chlorination of the silane.

In the chlorination of diphenyldichlorosilane (in presence of catalysts) it was found that only in the case of chlorination to the monochloro derivative is a pure compound formed – (p-chlorophenyl)-phenyldichlorosilane. With higher degrees of chlorination, mixtures of isomers of di-, tri-, tetra-, penta- or hexachlorodiphenyldichlorosilanes are formed.

The mono-, di- and trichlorinated derivatives of diphenyldichlorosilane are colorless, mobile, oily liquids; the tetrachloro derivative is a white crystalline substance (needles), and the penta- and hexachloro derivatives are viscous, oily, light-yellow transparent liquids.

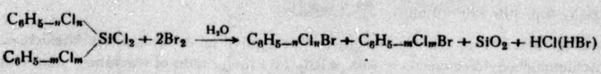
All the chlorodiphenyldichlorosilanes possess a sharp odor and fume in the air, but to a considerably lesser degree than chlorophenyltrichlorosilanes; they distil in vacuum without decomposition and are readily soluble in the majority of common organic solvents.

The structure of the chlorodiphenyldichlorosilanes was investigated by subjecting them to cleavage both with $AlCl_3$ and with bromine water.



$$\begin{array}{l} C_6H_{5-n}Cl_n \\ C_6H_{5-m}Cl_m \end{array} SiCl_2 + AlCl_3 \xrightarrow{H_2O} C_6H_{5-m}Cl_mSiCl_3 + C_6H_{6-n}Cl_n + HCl$$

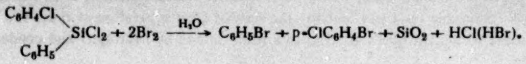
$$C_6H_{5-m}Cl_mSiCl_3 \xrightarrow[+H_2O]{+AlCl_3} C_6H_{6-m}Cl_m + SiO_2 + HCl$$



$$\begin{array}{l} C_6H_{5-n}Cl_n \\ C_6H_{5-m}Cl_m \end{array} SiCl_2 + 2Br_2 \xrightarrow{H_2O} C_6H_{5-n}Cl_nBr + C_6H_{5-m}Cl_mBr + SiO_2 + HCl(HBr)$$

The structure of the resultant chloro and bromo derivatives of benzene enabled establishment, just as in the case of chlorophenyltrichlorosilanes, not only of the position of the chlorine atoms in the aromatic rings but also of the orientating effect of the $ArSiCl_2$ group.

When the monochlorodiphenyldichlorosilane obtained by chlorination of diphenyldichlorosilane is cleaved with bromine water, p-bromochlorobenzene (yield about 40%) is obtained instead of m-bromochlorobenzene; the other product of cleavage is bromobenzene (yield 72%):

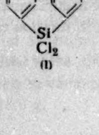


$$\begin{array}{l} C_6H_4Cl \\ C_6H_5 \end{array} SiCl_2 + 2Br_2 \xrightarrow{H_2O} C_6H_5Br + p\text{-}ClC_6H_4Br + SiO_2 + HCl(HBr).$$

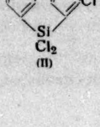
The structure of the isolated cleavage products indicates that the chlorine atom enters the ring in the para-position to the silicon atom, so that the chlorodiphenyldichlorosilane formed is (p-chlorophenyl)-phenyldichlorosilane. This structure was confirmed by the fact that the prepared substance is identical with synthetic (p-chlorophenyl)-phenyldichlorosilane that we obtained from phenyl magnesium bromide and p-chlorophenyltrichlorosilane.

Consequently, the anomalous orientation by the silicon atom (linked with electronegative atoms and an aromatic nucleus) of substituents entering the ring was observed not only in the case of phenyltrichlorosilane but also in that of diphenyldichlorosilane. This was further confirmed by the structure of dichlorodiphenyldichlorosilane.

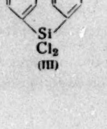
Determination of the structure of the dichlorodiphenyldichlorosilane, obtained by chlorination of diphenyldichlorosilane, proved a more complicated problem. The following five isomers are actually possible when a second chlorine atom enters the molecule of (p-chlorophenyl)-phenyldichlorosilane:



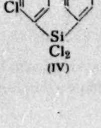
(I)



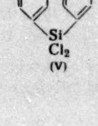
(II)



(III)



(IV)



(V)

Bearing in mind the anomalous orienting effect of the > $SiCl_2$ group, the most probable products of chlorination could be the dichlorides of structure (I), (II) and (IV).

Substances with structures (I) and (IV) that we obtained with the help of the organomagnesium synthesis according to the schemes:

$$2p\text{-}ClC_6H_4MgBr + SiCl_4 \rightarrow (p\text{-}ClC_6H_4)_2SiCl_2 + 2MgBrCl,$$

$$C_6H_5MgBr + 2,4\text{-}Cl_2C_6H_3SiCl_3 \rightarrow (C_6H_5)(2,4\text{-}Cl_2C_6H_3)SiCl_2 + MgBrCl,$$

proved to be not identical with the dichloride formed by chlorination of diphenyldichlorosilane, as is evident from a comparison of the constants of these compounds:

$(p\text{-}ClC_6H_4)_2SiCl_2$, b.p. 180-182° (7 mm), m.p. 54.7°, d_4^{20} 1.3880.

$(C_6H_5)(2,4\text{-}Cl_2C_6H_3)SiCl_2$, b.p. 172-174° (7 mm), d_4^{20} 1.3979.

$C_{12}H_8Cl_2SiCl_2$, b.p. 175-179° (7 mm), d_4^{20} 1.3955.

Hence, as in the other cases, cleavage reactions were applied for determination of structure. The products of cleavage of dichlorodiphenyldichlorosilane with $AlCl_3$ (1:1 molar ratio of reactants) were chlorobenzene and m-dichlorobenzene, which were obtained in total yield of 50%:

$$C_{12}H_8Cl_2SiCl_2 + AlCl_3 \xrightarrow{H_2O} C_6H_5Cl + m\text{-}C_6H_4Cl_2 + HCl + \text{resin}.$$

m-Dichlorobenzene was identified from its constants and its nitro derivative (1-nitro-2,4-dichlorobenzene), obtained in 67.6% yield.

The cleavage products obtained by treatment of dichlorodiphenyldichlorosilane with bromine water were bromobenzene and p-chlorobromobenzene, which were obtained in total yield of 80%, about $^2/_3$ being bromobenzene. A chlorine-containing resin was found in the residue after separation of these two benzene derivatives; its analysis corresponded to $(C_6H_3Cl_2SiO_{1.5})_n$, i.e. to a resin formed by hydrolysis and condensation of dichlorophenyltrichlorosilane.

The latter and the resin derived from it are – as indicated earlier [1] – not amenable to cleavage under the action of bromine water:

$$C_{12}H_8Cl_2SiCl_2 + 2Br_2 \xrightarrow{H_2O} C_6H_5Br + p\text{-}ClC_6H_4Br + \\ + (C_6H_3Cl_2SiO_{1.5})_n + HCl(HBr).$$

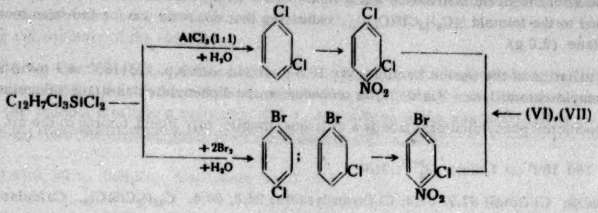
These data show that the dichlorodiphenyldichlorosilane under consideration is a mixture of the two isomers (I) and (IV), isomer (IV) predominating.

Similarly, by cleavage with aluminum chloride and bromine water, the structure and composition of the mixtures of isomers of tri-, tetra-, penta- and hexachlorodiphenyldichlorosilanes, obtained in the respective chlorination reactions, were established.

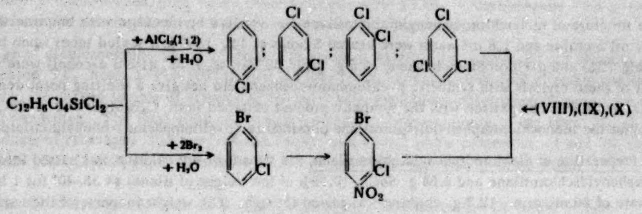
Results of cleavage reactions of these polychlorodiphenyldichlorosilanes are shown in the schemes presented below. In these schemes the last structural formulas show the structure and composition of the products of chlorination of chlorodiphenyldichlorosilanes as established by the composition and structure of the products of cleavage.

These data show that, starting from the trichloro derivative, the chlorine atoms entering the phenyl nuclei replace hydrogen atoms both in the ortho- and para- and in the meta-position in relation to the silicon atom.

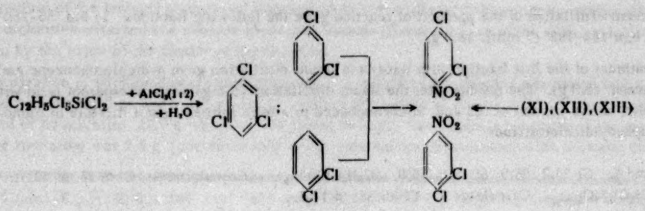
The structure of the compounds present in the mixtures of di-, tri-, tetra-, penta- and hexachlorodiphenyldichlorosilanes and their approximate composition have thus been established.



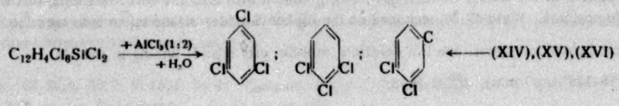
$C_{12}H_7Cl_3SiCl_2$
$AlCl_3$(1:1)
$+H_2O$
$+2Br_2$
$+H_2O$
Cl
Br
NO_2
(VI),(VII)



$C_{12}H_6Cl_4SiCl_2$
$+AlCl_3$(1:2)
$+H_2O$
$+2Br_2$
$+H_2O$
Cl
Br
NO_2
(VIII),(IX),(X)



$C_{12}H_5Cl_5SiCl_2$
$+AlCl_3$(1:2)
$+H_2O$
Cl
NO_2
(XI),(XII),(XIII)



$C_{12}H_4Cl_6SiCl_2$
$+AlCl_3$(1:2)
$+H_2O$
Cl
C
(XIV),(XV),(XVI)

These mixtures of isomers of chlorodiphenyldichlorosilanes of one particular degree of chlorination boil in a narrow temperature range, and therefore all attempts at their fractionation naturally failed to give positive results. Even attempted fractionation by freezing was unsuccessful in the simplest case of the dichlorodiphenyldichlorosilanes, consisting of a mixture of only two isomers, one of which – p, p'-dichlorodiphenyldichlorosilane – is a crystalline substance.

EXPERIMENTAL

I. Preparation of (p-chlorophenyl)-phenyldichlorosilane. A stream of dry chlorine was passed into a mixture of 20 g diphenyldichlorosilane and 0.04 g $SbCl_3$ (0.2% of the weight of the silane) at 35-40° for 40 minutes at a speed of 50 ml/min. The resultant increase in weight of the reaction mass was 3.0 g (compared with the calculated value of 2.7 g). The amount of chlorine passed through was 6.2 g. Distillation of the chlorination products in vacuum gave the following fractions: 1) b.p. 50-150° (at 7 mm), 3.2 g; 2) b.p. 150-167° (at 7 mm), 18.0 g.

p-Dichlorobenzene was isolated by treatment of the first fraction with water and distillation with steam. The residue after the steam distillation was a light-yellow transparent resin whose analysis for Cl and Si corresponded to the formula $(C_6H_4ClSiO_{1.5})_n$, indicating that this resin was formed from monochlorophenyltrichlorosilane (2.0 g).

Redistillation of the second fraction gave 16.5 g liquid with b.p. 158-163° at 7 mm; this was monochlorodiphenyldichlorosilane. Yield 72.7% reckoned on the diphenyldichlorosilane taken into reaction.

Monochlorodiphenyldichlorosilane is a colorless, mobile, oily liquid, fuming in the air.

B.p. 160-162° (at 7 mm), d_4^{20} 1.3190.

Found %: Cl (total) 37.2, 37.4; Cl (hydrolyzable) 24.5, 24.4. $C_{12}H_9ClSiCl_2$. Calculated %: Cl (total) 37.04; Cl (hydrolyzable) 24.7.

The structure of monochlorodiphenyldichlorosilane was verified by cleavage with bromine water (2.0 g silane, 0.7 ml bromine and 1.8 ml water were heated 5 hours at 140-150° in a sealed tube) when bromobenzene (0.8 g, yield 72%) and p-chlorobromobenzene (0.5 g, yield 38.5%), m.p. 65° (from alcohol) were isolated; a mixed test of these crystals with synthetic p-chlorobromobenzene did not give a melting point depression. These data, as well as comparison with the synthetic product obtained from C_6H_5MgBr and $p\text{-}ClC_6H_4SiCl_3$,* indicated that the monochlorodiphenyldichlorosilane obtained is (p-chlorophenyl)-phenyldichlorosilane.

II. Preparation of dichlorodiphenyldichlorosilane. A stream of dry chlorine was passed into a mixture of 20 g diphenyldichlorosilane and 0.04 g $SbCl_3$ (0.02% of the weight of silane) at 35-40° for 1 hour 20 minutes at a rate of 50 ml/min. 12.7 g chlorine was passed through. The weight increase of the reaction mass after passage of the gas was 6.2 g (compared with 5.4 g required for chlorination to the dichloro derivative.

Vacuum distillation of the products of reaction gave the following fractions: 1) b.p. 55-150° (7 mm), 6.0 g; 2) b.p. 150-195° (7 mm), 18.9 g.

Treatment of the first fraction with water and steam distillation gave p-dichlorobenzene and 1,2,4-trichlorobenzene (2.3 g). The residue after the steam distillation (2.5 g) was a transparent resin with a light yellow color, whose content of Cl and Si corresponded to a resin formed from a mixture of mono- and dichlorodiphenyldichlorosilanes.

Found %: Cl 26.7, 26.9; Si 15.8, 16.0. $(C_6H_4ClSiO_{1.5})_n$. Calculated %: Cl 21.7; Si 17.1. $(C_6H_3Cl_2SiO_{1.5})_n$. Calculated %: Cl 35.85; Si 14.1.

Redistillation of the second fraction gave 14.6 g liquid with b.p. 173-181° at 7 mm; this was dichlorodiphenyldichlorosilane. Yield 57.5% reckoned on the diphenyldichlorosilane taken into reaction.

Dichlorodiphenyldichlorosilane is a colorless, mobile, oily liquid, fuming in the air.

B.p. 175-179° (at 7 mm), d_4^{20} 1.3955.

Found %: Cl (total) 43.8, 43.9; Cl (hydrolyzable) 22.0, 21.8. $C_{12}H_8Cl_2SiCl_2$.
Calculated %: Cl (total) 44.1; Cl (hydrolyzable) 22.05.

A secondary product of the reaction was monochlorodiphenyldichlorosilane (b.p. 158-162° at 7 mm), isolated by redistillation of the second fraction (4.0 g). Total yield of chlorodiphenyldichlorosilanes 76.2%.

The properties of the dichlorodiphenyldichlorosilane obtained were not identical with those of the synthetic p,p'-dichloro derivative obtained from $p\text{-}ClC_6H_4MgBr$ and $SiCl_4$ (b.p. 180-182° at 7 mm, d_4^{20} 1.3880, m.p. 54.7°), nor with those of (2,4-dichlorophenyl)-phenyldichlorosilane that we synthesized for the first time from C_6H_5MgBr and 2,4-dichlorophenyltrichlorosilane.* The dichlorodiphenyldichlorosilane obtained by chlorination did not crystallize either on freezing (–60°) or on seeding with synthetic p,p'-dichlorodiphenyldichlorosilane; consequently, the latter was subjected to cleavage with $AlCl_3$ and bromine water for the purpose of establishing the structure of the chloride.

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*Into 7 g $p\text{-}ClC_6H_4SiCl_3$ was run an ethereal solution of organomagnesium compound prepared from 5 g bromobenzene and 0.9 g magnesium, and the mixture was heated $1\frac{1}{2}$ hours at 50-60°. Fractionation of the mixture gave a fraction (4.8 g) with b.p. 160-162° at 7 mm and d_4^{20} 1.3187; this was (p-chlorophenyl)-phenyldichlorosilane. Yield 60% on the p-chlorophenyltrichlorosilane taken into reaction.

A mixture of 6.0 g dichlorodiphenyldichlorosilane and 2.6 g $AlCl_3$ was kept with stirring for 3 hours at 50° and for 27 hours at 25-30° (the mixture acquired a dark red color), decomposed with water and distilled with steam. From the aqueous distillate a substance (0.7 g) was isolated which was identified as m-dichlorobenzene (yield 40.0%) from the melting point (–25°) and density (d_4^{20} 1.2890).

Found %: Cl 47.6, 47.8. $C_6H_4Cl_2$. Calculated %: Cl 48.3.

The m-dichlorobenzene was identified by conversion with nitration mixture into a nitro derivative which was 2,4-dichloro-1-nitrobenzene, m.p. 33.1° (from alcohol), yield 67.6%. Chlorobenzene (0.4 g, yield 50.0%) was separated from the aqueous distillate together with the m-dichlorobenzene.

Cleavage of dichlorodiphenyldichlorosilane with bromine water (3.3 g silane, 1.1 ml bromine and 3.0 ml water were heated 7 1/2 hours at 170-180° in a sealed tube) gave bromobenzene (0.8 g) and p-chlorobromobenzene (0.5 g). A mixed sample of crystals of the latter with synthetic p-chlorobromobenzene did not give a melting point depression. The total yield of bromine-containing cleavage products was about 2/3 of the total weight of products of cleavage. The non-volatile residue was a resin whose content of Cl and Si indicated the composition $(C_6H_3Cl_2SiO_{1.5})_n$. This resin did not undergo cleavage with bromine water.

Found %: Cl 35.1, 35.4; Si 14.0, 13.8. $(C_6H_3Cl_2SiO_{1.5})_n$. Calculated %: Cl 35.85; Si 14.1.

The structure of the isolated products of cleavage of dichlorodiphenyldichlorosilane justifies the assumption that the dichloride obtained is a mixture of the two isomers (I) and (IV), in which (IV) predominates (as indicated also by the value of the density of the chloride).

III. Preparation of trichlorodiphenyldichlorosilane. A stream of dry chlorine was passed into a mixture of 15 g diphenyldichlorosilane and 0.045 g $SbCl_3$ (0.3% of the weight of silane) at 50-55° for 1 hour 40 minutes at a speed of 50 ml/min. 15.8 g chlorine was passed through. The increase in weight of the reaction mass after the treatment was 7.5 g (compared with 6.1 g required for chlorination to the trichloro derivative).

After distillation of the chlorination products in vacuum the following fractions were obtained: 1) b.p. 50-150° (at 7 mm), 8.3 g; 2) b.p. 150-210° (at 7 mm), 12.7 g. The first fraction crystallized during distillation. Trichlorobenzene (3 g) was isolated after treatment with water and steam distillation. The unsharp melting point of the crystals (40-58°) indicated the presence of a mixture of isomers of trichlorobenzene. The non-volatile residue was a transparent resin whose Cl and Si content indicated that it consisted of a mixture of mono- and dichlorophenyltrichlorosilanes.

Found %: Cl 30.4, 30.7; Si 15.0, 14.9. $(C_6H_4ClSiO_{1.5})_n$. Calculated %: Cl 21.7; Si 17.1.
$(C_6H_3Cl_2SiO_{1.5})_n$. Calculated %: Cl 35.85; Si 14.1.

Redistillation of the second fraction gave 10.5 g liquid with b.p. 192-201° at 7 mm; this was trichlorodiphenyldichlorosilane. Yield 50.0% reckoned on the diphenyldichlorosilane taken into the reaction.

Trichlorodiphenyldichlorosilane is a colorless, mobile, oily liquid, fuming in the air.

B.p. 194-200° (at 7 mm), d_4^{20} 1.4926.

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*To 7.8 g 2,4-dichlorophenyltrichlorosilane with cooling was added a solution of organomagnesium compound prepared from 4.5 g bromobenzene and 0.8 g magnesium, and the mixture was heated 1 1/2 hours at 50-60°. Fractionation of the mixture gave a fraction (4.8 g) with b.p. 172-174° at 7 mm and d_4^{20} 1.3979; this was (2,4 dichlorophenyl)-phenyldichlorosilane.
Found %: Cl (total) 44.3, 43.8; Cl (hydrolyzable) 21.7, 21.8. $C_{12}H_8Cl_2SiCl_2$. Calculated %: Cl (total) 44.1; Cl (hydrolyzable) 22.05. Yield 53.2% reckoned on the 2,4-dichlorophenyltrichlorosilane taken into reaction.

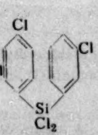
Found %: Cl (total) 49.4, 49.3; Cl (hydrolyzable) 20.0, 20.4. $C_{12}H_7Cl_3SiCl_2$. Calculated %: Cl (total) 49.8; Cl (hydrolyzable) 19.9.

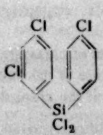
A by-product of the reaction was tetrachlorodiphenyldichlorosilane (b.p. 209-211° at 7 mm), isolated on redistillation of the second fraction (2.0 g). The total yield of chlorodiphenyldichlorosilanes was 60.5%.

The structure of the prepared trichlorodiphenyldichlorosilane was established by subjecting it to cleavage with $AlCl_3$ and bromine water. Reaction of this silane with $AlCl_3$ was effected by a procedure similar to that for the dichloro derivative. The product of reaction of trichlorodiphenyldichlorosilane with $AlCl_3$ (1:1 molar ratio) was m-dichlorobenzene (yield 40%). In addition a resin with the composition $(C_6H_4ClSiO_{1.5})_n$ was isolated. The m-dichlorobenzene was identified by nitration which gave 1-nitro-2,4-dichlorobenzene with m.p. 32-33° (from alcohol).

Cleavage of trichlorodiphenyldichlorosilane with bromine water (4.0 g silane, 1.4 ml bromine and 3.6 ml water were heated $7\,^1/_2$ hours at 170-180° in a sealed tube) gave p-chlorobromobenzene (0.7 g) and m-chlorobromobenzene (1.0 g). The latter was identified by conversion to the nitro derivative which proved to be 2-chloro-4-bromo-1-nitrobenzene with m.p. 44° (from alcohol). The total yield of products of cleavage of trichlorodiphenyldichlorosilane with bromine water was 80%, of which about $^2/_3$ was m-chlorobromobenzene. The non-volatile residue after cleavage was a resin whose Cl and Si content corresponded to the formula $(C_6H_3Cl_2SiO_{1.5})_n$.

On the basis of the foregoing data we can assume that the trichlorodiphenyldichlorosilane obtained by chlorination of diphenyldichlorosilane in presence of catalysts is a mixture of isomers (VI) and (VII), in which isomer (VI) predominates.


(VI)


(VII)

IV. Preparation of tetrachlorodiphenyldichlorosilane. A stream of dry chlorine was passed into a mixture of 30 g diphenyldichlorosilane and 0.09 g $SbCl_3$ (0.3% of the weight of silane) for 6 hours at a speed of 40 ml//min. During the first 3 hours the temperature was 50-55°, and for the remaining period 70-75°. 46.0 g chlorine was passed in. The increase in weight of the reaction mass after treatment was 22.0 g (compared with 16.3 g required for chlorination to the tetrachloro derivative). The product of chlorination crystallized on cooling (needles). Its distillation in vacuum gave the following fractions: 1) b.p. 80-160° (at 7 mm), 21.0 g; 2) b.p. 160-215° (at 7 mm), 28.0 g. The first fraction crystallized on distillation. Its treatment with water and steam distillation gave a mixture of tri- and tetrachlorobenzenes (8.3 g) with m.p. 52-69°. The non-volatile residue was a light-yellow resin consisting mainly of dichlorodiphenyltrichlorosilane.

Found %: Cl 36.8, 36.7; Si 13.6, 13.7. $(C_6H_3Cl_2SiO_{1.5})_n$. Calculated %: Cl 35.85; Si 14.1.

Redistillation of the second fraction gave 19.0 g liquid with b.p. 209-215° at 7 mm, which crystallized on cooling with formation of needles of tetrachlorodiphenyldichlorosilane.

Tetrachlorodiphenyldichlorosilane is a white crystalline substance, fuming in the air; needles (from ligroine) with m.p. 89-93°, b.p. 210-214° at 7 mm.

Found %: Cl (total) 54.1, 54.3; Cl (hydrolyzable) 18.4, 18.0. $C_{12}H_6Cl_4SiCl_2$. Calculated %: Cl (total) 54.5; Cl (hydrolyzable) 18.2.

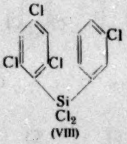
A by-product of the reaction was pentachlorodiphenyldichlorosilane (8.0 g) – a viscous, oily liquid with a light yellow color and b.p. 220-225° at 7 mm, not crystallizing on cooling. Total yield of chlorodiphenyldichlorosilanes 59.5%.

The structure of the prepared tetrachloro derivative was verified by cleavage with $AlCl_3$ and bromine water by the above-described procedure. The products of complete cleavage of tetrachlorodiphenyldichlorosilane with $AlCl_3$ (1:1 molar ratio) were chlorobenzene, 1,3,5-trichlorobenzene and a mixture of o- and m-dichlorobenzenes whose chlorine contents were in good agreement with the theoretical amounts.

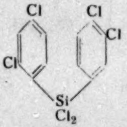
Cleavage of tetrachlorodiphenyldichlorosilane with bromine water (2.0 g silane, 0.7 ml bromine and 1.8 ml water were heated 5½ hours at 160-170° and 4 hours at 190-200° in a sealed tube) gave m-chlorobromobenzene (0.8 g), yield approximately 50%. Nitration of the latter led to 2-chloro-4-bromo-1-nitrobenzene, m.p. 44.7° (from alcohol). The non-volatile residue after cleavage was a transparent, light-yellow resin whose Cl and Si contents indicated that it comprised a mixture of $C_6H_2Cl_3SiCl_3$ and $C_{12}H_6Cl_4SiCl_2$. This type of resin is not susceptible to cleavage by bromine water.

Found %: Cl 43.8, 44.0; Si 9.9, 10.1. $(C_{12}H_6Cl_4SiO)_n$. Calculated %: Cl 42.26; Si 8.3. $(C_6H_2Cl_3SiO_{1.5})_n$. Calculated %: Cl 45.8; Si 12.04.

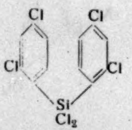
On the basis of the structure of the isolated products of cleavage of tetrachlorodiphenyldichlorosilane, it follows that the latter is a mixture of isomers (VIII), (IX) and (X).



(VIII)



(IX)



(X)

V. Preparation of penta- and hexachlorodiphenyldichlorosilanes. A stream of dry chlorine was passed into a mixture of 25 g diphenyldichlorosilane and 0.1 g $SbCl_3$ (0.4% on the weight of silane) at a speed of 40 ml/min. Chlorination required 6½ hours, the temperature being held at 45-50° for the first hour, at 55-60° for the second, at 65-70° for the third, at 75-80° for the fourth, and thereafter at 80-85°.

The amount of chlorine passed in was 50.0 g. The increase in weight of the reaction mass at the end was 19.0 g (against 20.4 g required for chlorination to the hexachloro derivative). The product of chlorination partly crystallized on progressive cooling (needles). Its distillation in vacuum gave the following fractions: 1) b.p. 90-160° (7 mm), 19.0 g; 2) b.p. 160-240° (7 mm), 22.0 g.

The first fraction crystallized completely on distillation. Its treatment with water and steam distillation gave a mixture of tri- and tetrachlorobenzenes (6.2 g), the second predominating (m.p. 118-130°). The non-volatile residue was a light-yellow resin whose content of Cl and Si corresponded to a mixture of dichloro- and trichlorophenyltrichlorosilanes.

Found %: Cl 41.6, 41.3; Si 12.8, 12.7. $(C_6H_3Cl_2SiO_{1.5})_n$. Calculated %: Cl 35.85; Si 14.1. $(C_6H_2Cl_3SiO_{1.5})_n$. Calculated %: Cl 45.8; Si 12.04.

Redistillation of the second fraction yielded 12.0 g viscous, light-yellow liquid with b.p. 220-224° at 6 mm and d_4^{20} 1.6203, consisting of pentachlorodiphenyldichlorosilane.

Found %: Cl (total) 57.9, 58.2; Cl (hydrolyzable) 16.9, 16.6. $C_{12}H_5Cl_5SiCl_2$. Calculated %: Cl (total) 58.4; Cl (hydrolyzable) 16.7.

The same second fraction gave 8.5 g of a viscous, substantially non-mobile, yellow mass with b.p. 231-235° at 7 mm, d_4^{20} 1.5901, consisting of hexachlorodiphenyldichlorosilane.

Found %: Cl (total) 61.1, 60.9; Cl (hydrolyzable) 15.8, 15.9. $C_{12}H_4Cl_6SiCl_2$. Calculated %: Cl (total 61.7; Cl (hydrolyzable) 15.4.

The total yield of polychlorodiphenyldichlorosilanes was 54.0%.

The structure of the prepared penta- and hexachloro derivatives of diphenyldichlorosilane was verified by cleavage with $AlCl_3$ (1:2 molar ratio of reactants) by the procedure described above.

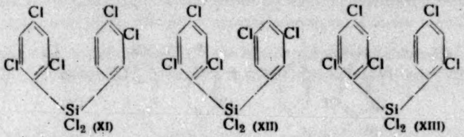
Bromine water does not cleave these silanes even after prolonged heating in a sealed tube at 200°.

The products of cleavage of pentachlorodiphenyldichlorosilane with $AlCl_3$ were 1,3,5-trichlorobenzene (m.p. 63°), m- and o-dichlorobenzene, which were identified by conversion to the corresponding nitro derivatives.

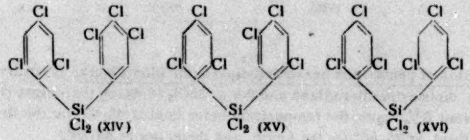
A product of cleavage of hexachlorodiphenyldichlorosilane with $AlCl_3$ was trichlorobenzene with a gradual melting point (57-62°), which indicated that it was a mixture of 1,2,3- and 1,3,5-trichlorobenzenes (1,2,3-trichlorobenzene, m.p. 53-54°; 1,3,5-trichlorobenzene, m.p. 63.4°). Another product of cleavage was 1,2,4-trichlorobenzene with m.p. 17.5°. The yield of cleavage products was approximately 40%.

The structure of the separated products of cleavage indicate that pentachloro- (A) and hexachlorodiphenyldichlorosilanes (B) are a mixture of the following isomers:

(A)



(B)



Experiments on chlorination of diphenyldichlorosilane in presence of other catalysts (Fe, $AlCl_3$, iodine, PCl_5), listed in the table, were performed by a procedure similar to that for chlorination of diphenyldichlorosilane in presence of $SbCl_3$.

SUMMARY

1. Chloro derivatives of diphenyldichlorosilane ranging from monochloro to hexachloro derivatives can be obtained by chlorination of diphenyldichlorosilane in presence of the usual catalysts for chlorination of aromatic compounds ($AlCl_3$, $FeCl_3$, $SbCl_3$, iodine).

2. It was established that, depending upon the nature of the catalyst, the process of chlorination is accompanied to a greater or lesser degree by a secondary process of destructive chlorination which leads to formation of products of cleavage of diphenyldichlorosilane and its chloro derivatives. The least cleavage during preparation of polychloro derivatives is observed when using antimony trichloride as catalyst.

3. It is found that only in the case of chlorination to the monochloro derivative is a pure substance formed – (p-chlorophenyl)-phenyldichlorosilane. With more far-reaching chlorination to di-, tri-, etc. chloro derivatives, non-resolvable mixtures of isomers are formed which boil in a narrow temperature range.

4. Cleavage of the prepared mixtures of isomers with aluminum chloride or bromine water was used to establish the structure of the compounds present in the mixtures of di-, tri-, tetra-, penta- and hexachlorodiphenyldichlorosilanes and the approximate composition of these mixtures.

5. It is found that the phenyldichlorosilyl group, like the $SiCl_3$ group, directs the chlorine atoms entering the ring during chlorination of diphenyldichlorosilane in presence of a catalyst, not into the meta- position but

into the ortho- and para- positions. This directivity persists until two atoms of chlorine have entered the phenyl rings. On further chlorination the chlorine atoms replace hydrogen atoms in ortho-, para- and meta- positions.

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[3] A. Ya. Yakubovich and G. V. Motsarev, Proc. Acad. Sci. USSR 91, 277 (1953).

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Received September 9, 1955

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*T.p. = C. B. Translation pagination.

THE ANOMALOUS REACTION OF α-HALOKETONES WITH ESTERS OF PHOSPHOROUS ACID

II. REACTION OF CHLORO- AND BROMOACETONE WITH ESTERS OF PHOSPHOROUS AND PHENYLPHOSPHINOUS ACIDS

A. N. Pudovik and V. P. Averyanova

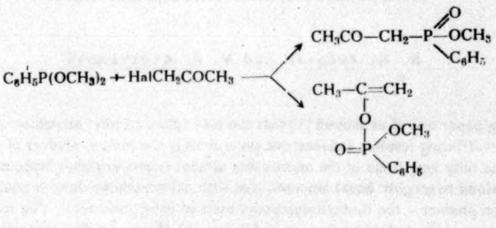
In the preceding paper one of us showed [1] that the reaction of triethyl phosphite with iodo-, bromo- and chloroacetone leads to differing results. Iodoacetone gives mainly the normal product of reaction – diethyl phosphonacetone – and only very little of the unsaturated diethyl isopropenylphosphoric ester; with bromoacetone both products are obtained in roughly equal amounts, and with chloroacetone there is predominant formation of the anomalous reaction product – the diethylisopropenyl ester of phosphoric acid. The reaction of chloroacetone with triethyl phosphite was also studied by Dawson and Burger [2] who report the preparation of diethyl phosphonacetone in 66% yield and do not mention the formation of diethylisopropenyl phosphoric ester.

Bearing in mind the very diverse results obtained by us and American chemists during study of this reaction, and considering their very great theoretical interest, we decided to study the reactions of chloro- and bromoacetone with a wider range of esters of phosphorous and phosphinous acids: trimethyl, triethyl, tri-n-butyl and triisobutyl phosphites and the methyl ester of phenylphosphinous acid. With trimethyl phosphite, triethyl phosphite and chloroacetone, the experiments were performed both at the lowest possible temperatures at which the reactions would go, and at the boiling point of the phosphorous esters. As we see from the table, the lower the temperature of the reaction mixture, the greater the extent to which the reaction proceeds anomalously with formation of dialkyl isopropenyl phosphoric ester. The amount of phosphonacetone in all the experiments varied between 5 and 19%. This regularity was observed to a still greater degree in reactions with bromoacetone. A marked influence of the nature of the halogen on the course of the reactions was observed in all reactions performed with different esters of phosphorous acid and with α-haloketones. Reactions at 135-160° with bromoacetone

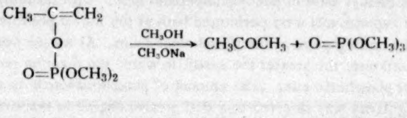
Phosphorous ester	Haloketone	Reaction conditions	Phosphinic ester/unsaturated phosphoric ester ratio (in %)		Total yield of reaction products (in % of theoretical)
			phosphinic ester	phosphoric ester	
$(CH_3O)_3P$	CH_3COCH_2Br	110—115°	44.5	55.5	71.0
	CH_3COCH_2Cl	70—80	5.3	94.7	70.5
	CH_3COCH_2Cl	110—115	16.5	83.5	80.0
$(C_2H_5O)_3P$	CH_3COCH_2I	In ethereal solution	90.0	10.0	82.6
	CH_3COCH_2Br	In ethereal solution	19.9	80.1	66.3
	CH_3COCH_2Br	150—160°	80.0	20.0	81.8
	CH_3COCH_2Cl	100—120	6.1	93.9	60.0
	CH_3COCH_2Cl	155—160	11.9	88.1	75.6
$(n\text{-}C_4H_9O)_3P$	CH_3COCH_2Br	145—155	64.7	35.3	71.6
	CH_3COCH_2Cl	135—145	13.7	86.3	61.0
$(iso\text{-}C_4H_9O)_3P$	CH_3COCH_2Br	150—155	79.1	20.9	60.0
	CH_3COCH_2Cl	115—125	6.3	93.7	78.4
	CH_3COCH_2Cl	150—160	18.9	81.1	70.0

leads to formation predominantly of esters of dialkylphosphinic acids, i.e. the reaction goes mainly by the normal mechanism of the Arbuzov rearrangement, while with chloroacetone the main reaction products are dialkylisopropenyl phosphoric esters, i.e. the reactions go mainly according to the anomalous mechanism.

Similar results were obtained also with the methyl ester of phenylphosphinous acid. The reactions with chloroacetone gave the methylisopropenyl ester of phenylphosphinic acid. With bromoacetone the reaction goes very energetically. Even addition of a few drops of bromoacetone to the methyl ester of phenylphosphinous acid heated to 80°, caused the temperature of the reaction mass to rise quickly to 200°. A large amount of resin was formed. The reaction goes quietly in ethereal solution ; both isomeric products are formed in approximately equal amounts.



The structure of some of the prepared products was confirmed by reactions of transesterification, saponification and ozonization. Transesterification of dimethylisopropenyl and diisobutylisopropenyl esters of phosphoric acid in solutions of methyl and isobutyl alcohols in presence of alkoxides led to good yields of acetone and, respectively, trimethyl phosphate and triisobutyl phosphate:



$$CH_3-\underset{\underset{O=P(OCH_3)_2}{|}}{\underset{O}{\underset{|}{C}}}=CH_2 \xrightarrow[CH_3ONa]{CH_3OH} CH_3COCH_3 + O=P(OCH_3)_3.$$

The reactions go with great facility. Ozonization of diethylisopropenyl phosphoric ester gave formaldehyde, which was identified by the reaction with β-naphthol and dimedon. Finally, we studied the reactions of chloro- and bromoacetone with sodium diethyl phosphite. The reactions with bromoacetone in solution in ligroine and ether go very easily but lead to formation of a mixture of products boiling over a wide range. By several fractionations we isolated diethyl phosphonacetone with b.p. 131° at 11 mm and n_D^{20} 1.4320. Its yield in both experiments was only 15%. Similar experiments in solution in benzene and toluene likewise led to fractions with a wide boiling range; pure phosphonacetone could not be separated in any experiment.

The reaction of sodium diethyl phosphite is still more complex; a fraction corresponding to diethylphosphonacetone was obtained in a yield of only 5.7%; the remainder consisted of lower boiling fractions.

EXPERIMENTAL

Action of trimethyl phosphite on bromoacetone. The reaction was carried out in an Arbuzov flask with 20 g trimethyl phosphite and 22.1 g bromoacetone. The latter was added dropwise to the trimethyl phosphite, heated to 110-115°, at such a rate that the temperature of the reaction mixture was held at that level throughout the duration of the experiment. Later the reaction mixture was heated for half an hour at 120° and then fractionated in vacuum. Yield 10.5 g dimethylisopropenyl phosphite.

B.p. 84-85° at 9 mm, d_4^{20} 1.1449, n_D^{20} 1.4175, MR_D 36.50; calc. 36.81.
Found %: P 18.62, 18.58. $C_5H_{11}O_4P$. Calculated %: P 18.66.

In addition 8.4 g dimethyl phosphonacetone was obtained.

B.p. 123-124° at 10 mm, d_4^{20} 1.1748, n_D^{20} 1.4337, MR_D 36.76; calc. 36.17.
Found %: P 18.26, 18.33. $C_5H_{11}O_4P$. Calculated %: P 18.66.

Action of trimethyl phosphite on chloroacetone. Experiment I. A reaction mixture comprising 34 g trimethyl phosphite and 25.2 chloroacetone, in an Arbuzov flask, was gradually heated on a water bath. Reaction commenced at 70°, as signalized by rapid temperature rise and by copious evolution of methyl chloride. The flask was cooled with water and the temperature held at not higher than 80°. After methyl chloride had ceased to come off, the reaction mixture was fractionated in vacuum to give 30 g dimethylisopropenyl phosphate with b.p. 84-86° at 10 mm, n_D^{20} 1.4165, and 1.7 g dimethyl phosphonacetone with b.p. 125-127° at 12 mm, n_D^{20} 1.4340.

Experiment II. The experiment was performed with 30 g trimethyl phosphite and 22.7 g chloroacetone at 110°. Yield 25.4 g dimethylisopropenyl phosphate and 6.6 g dimethyl phosphonacetone.

Transesterification of isopropenyl dimethyl phosphate. To an alcoholic solution of sodium methoxide, prepared from 0.2 g sodium and 15 ml anhydrous methyl alcohol, was added 10 g isopropenyldimethyl phosphate. The methyl alcohol and acetone were driven off by heating on a water bath. From the first 12 ml of distillate was obtained 1.2 g acetone semicarbazone with m.p. 186° (mixed melting test). Fractionation of the residue gave 2.5 g trimethyl phosphite with b.p. 72-73° at 10 mm, n_D^{20} 1.4000.

Action of triethyl phosphite on chloroacetone. Experiment I. A reaction mixture of 40 g triethyl phosphite and 22 g chloroacetone was gradually heated. Ethyl bromide started to come off at 95°. The reaction was brought to an end by heating the mixture at 110-120° for 30 minutes. Fractionation in vacuum gave 26 g diethylisopropenyl phosphate and 1.7 g diethyl phosphonacetone with b.p. 127-129° at 10 mm, n_D^{20} 1.4350.

Experiment II. 13.8 g chloroacetone was gradually added to 25 g boiling triethyl phosphite (b.p. 156°). Yield 2.7 g diethyl phosphonacetone and 20 g diethylisopropenyl phosphate.

Ozonization of diethylisopropenyl phosphate. Through a solution of 6 g diethylisopropenyl phosphate in 20 ml carbon tetrachloride, cooled with iced water, was passed ozonized oxygen for 14 hours. After removal of the carbon tetrachloride in vacuum, the ozonide was covered with ether and left for 24 hours at room temperature. The ozonide was decomposed by heating with 50 ml water on a water bath. The formaldehyde in the first 20 ml distillate was detected by reactions with β-naphthol,, which gave pink crystals with m.p. 196° (mixed test m.p. 197°), and with dimedon, which gave colorless needles with m.p. 189° (m.p. in mixed test 189-190°).

Action of tri-n-butyl phosphite on chloroacetone. The reaction was performed with 30 g tri-n-butyl phosphite and 11 g chloroacetone at 135-145°. Two fractionations yielded 15.8 g dibutylisopropenyl phosphate.

B.p. 125-126° at 5 mm, d_4^{20} 1.0049, n_D^{20} 1.4268, MR_D 64.1; calc. 64.52.
Found %: P 12.31, 12.16. $C_{11}H_{23}O_4P$. Calculated %: P 12.4.

In addition 2.5 g di-n-butyl phosphonacetone with b.p. 149-150° at 11 mm, n_D^{20} 1.4322, was isolated.

Action of tri-n-butyl phosphite on bromoacetone. 16.4 g bromoacetone was added to 30 g tri-n-butyl phosphite at 145-155°. 7.6 g di-n-butylisopropenyl phosphate and 13.9 g di-n-butyl phosphonacetone were obtained.

B.p. 137-138° at 3 mm, d_4^{20} 1.0152, n_D^{20} 1.4315, MR_D 63.88; calc. 63.87.
Found %: P 12.68, 12.54. $C_{11}H_{23}O_4P$. Calculated %: P 12.40.

Action of triisobutyl phosphite on chloroacetone and bromoacetone. Experiment I. Evolution of isobutyl chloride started at 115-120° when a mixture of 40 g triisobutyl phosphite and 15 g chloroacetone was heated. The temperature of the reaction mixture was later held at 125° until the end of the reaction. Yield 30 g diisobutylpropenyl phosphate.

B.p. 122-123° at 9 mm, d_4^{20} 0.9955, n_D^{20} 1.4245, MR_D 64.22; calc. 64.52.
Found %: P 12.72, 12.54. $C_{11}H_{23}O_4P$. Calculated %: P 12.40.

About 2 g diisobutyl phosphonacetone with b.p. 147° at 10 mm and n_D^{20} 1.4330 was also isolated.

Experiment II. The reaction was performed with the same amounts of reactants but at 150-160°. Yield 25.7 g diisobutylpropenyl phosphate and 6 g diisobutyl phosphonacetone.

Experiment III. 10.9 g bromoacetone was gradually added to 20 g triisobutyl phosphite at 150-155°. Two fractionations gave 2.5 g diisobutyl phosphate with b.p. 123-126° at 10 mm and 9.5 g diisobutyl phosphonacetone.

B. p. 133-134° at 4 mm, d_4^{20} 1.0246, n_D^{20} 1.4335, MR_D 63.55; calc. 63.88.
Found %: P 12.60, 12.63. $C_{11}H_{23}O_4P$. Calculated %: P 12.40.

Transesterification of diisobutylisopropenyl phosphate. To a solution of sodium isobutoxide, prepared in an Arbuzov flask from 15 ml anhydrous isobutyl alcohol and 0.2 g sodium, was added 10 g diisobutylisopropenyl phosphate. During heating of the reaction mixture on an oil bath about 2 g acetone came off (semicarbazone m.p. 188°); from the residue after distillation of the isobutyl alcohol was obtained 4.5 g triisobutyl phosphate with b.p. 134-135° at 10 mm; n_D^{20} 1.4195, d_4^{20} 0.9650.

Saponification of diisobutylisopropenyl phosphate. 10 g of the ester and 15 ml 30% sulfuric acid, in an Arbuzov flask, were heated on a water bath. Reaction commenced at once and went very stormily with considerable heat generation in the mass. A second fractionation gave 2.3 g acetone with b.p. 56-57° (semicarbazone with m.p. 186-187°).

Action of methyl ester of phenylphosphinous acid on chloroacetone and bromoacetone. Experiment I. To 28 g methyl ester of phenylphosphinous acid, contained in an Arbuzov flask and heated to 90°, was slowly added 15.2 g chloroacetone. The reaction went very stormily and was accompanied by considerable heat development in the reaction mixture. The rate of addition of the chloroacetone was so regulated that the temperature of the reaction mixture did not rise above 120-130°. Fractionation gave 18.5 g methylisopropenyl ester of phenylphosphinic acid.

B.p. 137-138° at 8 mm, d_4^{20} 1.1421, n_D^{20} 1.5120, MR_D 55.76; calc. 55.18.
Found %: P 14.47, 14.42. $C_{10}H_{13}O_3P$. Calculated %: P 14.60.

2.5 g of a fraction with b.p. 160-170° at 10 mm was also collected. On redistillation this gave 1.5 g fraction with b.p. 165-170° at 10 mm, n_D^{20} 1.5215.

Under similar conditions the reaction with bromoacetone resulted in resinification.

Experiment II. The reaction was performed with 20 g methyl ester of phenylphosphinous acid and 18 g bromoacetone in ether solution. The reaction went with great facility and was accompanied by steady evolution of methyl bromide. Fractionation gave 3.8 g methylisopropenyl ester of phenylphosphinic acid with b.p. 137-139° at 9 mm, n_D^{20} 1.5135, and 5 g methyl ester of phenylpropanoyl phosphinous acid.

B.p. 168-170° at 8 mm, d_4^{20} 1.1965, n_D^{20} 1.5220, MR_D 54.08; calc. 54.01.
Found %: P 14.45. $C_{10}H_{13}O_3P$. Calculated %: P 14.60.

A large quantity of resin remained in the flask.

Reaction of chloroacetone with sodium diethyl phosphite. To an ethereal solution of sodium diethyl phosphite, prepared from 100 g diethyl phosphorous acid and 14.4 g sodium in 200 ml ether, was slowly added 57.6 g chloroacetone. After 3 hours heating on a water bath and removal of part of the ether, the reaction mixture was centrifuged to remove the sodium chloride which came down in colloidal form. Fractionation gave fractions with b.p. 50-94° at 12 mm in the amount of 30 g, with b.p. 94-98° at 12 mm (6 g), and a fraction corresponding to phosphonacetone with b.p. 122-129° at 12 mm, n_D^{20} 1.4345 (7 g). Refractionations in a Widmer column of the lower boiling fractions failed to give any products with a constant boiling point.

Action of sodium diethyl phosphite on bromoacetone. To a ligroine solution of sodium diethyl phosphite, prepared from 50 g diethylphosphorous acid and 7 g sodium, was added 42.8 g bromoacetone. The reaction mixture was heated 3 hours on a water bath. Sodium bromide was removed by centrifuging. Fractionation gave 9 g diethylphosphonacetone with b.p. 131° at 11 mm, n_D^{20} 1.4320, and a series of lower boiling fractions. Similar reactions were performed in solution in ether, benzene and toluene without positive results.

SUMMARY

1. A study was made of reactions of chloro- and bromoacetone with trimethyl, triethyl, tri-n-butyl and triisobutyl phosphites, with the methyl ester of phenylphosphinous acid, and with sodium diethyl phosphite.

2. Reactions of bromoacetone and chloroacetone with esters of phosphorous and phosphinous acids give a mixture of the corresponding phosphonacetone, which is formed according to the Arbuzov rearrangement, and unsaturated phosphoric or phosphinic esters which are formed by an anomalous mechanism.

3. The main product in all reactions of esters of phosphorous and phosphinous acids with chloroacetone was the corresponding unsaturated phosphoric or phosphinic ester. The ethers of phosphonacetone are formed in minor amounts (their yields in the different reactions are 5 to 19%). The report of Dawson and Burger to the effect that diethyl phosphonacetone in 66% yield is the sole product of the reaction of triethyl phosphite with chloroacetone is not confirmed by our experiments.

4. Reaction of chloro- and bromoacetone with sodium diethyl phosphite in ligroine solution or ether solution gives diethyl phosphonacetone in 5-15% yields. No other pure products could be isolated in these reactions.

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Received June 7, 1955

Kazan State University

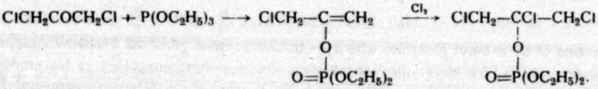
THE ANOMALOUS REACTION OF α-HALOKETONES WITH ESTERS OF PHOSPHOROUS ACID

III. THE REACTION OF α,α- AND α, γ-DIHALOKETONES WITH TRIETHYL PHOSPHITE

A. N. Pudovik and L. G. Salekhova

As was shown by one of us [1], the interaction of esters of phosphorous acid with haloacetones and with ω-haloacetophenones goes in two directions: according to Arbuzov rearrangement with formation of ketophosphinic acids and according to an anomalous mechanism with formation of unsaturated phosphoric esters. The ratio of the velocities of these reactions depends upon the nature of the halogen and upon the reaction temperature. In the present work we studied the reactions of esters of phosphorous acid, in particular triethyl phosphite, with α,α- and α, γ-dichloro- and dibromoacetones.

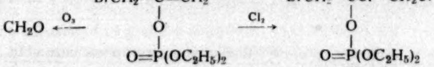
Reaction of triethyl phosphite with α, γ-dichloroacetone at 125-130° gave the 1-chloroisopropenyl-2-diethyl ester of phosphoric acid (I) in a yield of 44.8%. Chlorination (I) in carbon tetrachloride solution with good cooling led to an 85% yield of the 1,2,3-trichloroisopropyl-diethyl ester of phosphoric acid (II):



$$\mathrm{ClCH_2COCH_2Cl + P(OC_2H_5)_3 \longrightarrow ClCH_2{-}\underset{\substack{|\\ O\\ |\\ O{=}P(OC_2H_5)_2}}{C}{=}CH_2 \xrightarrow{Cl_2} ClCH_2{-}\underset{\substack{|\\ O\\ |\\ O{=}P(OC_2H_5)_2}}{CCl}{-}CH_2Cl}$$

(I) (II)

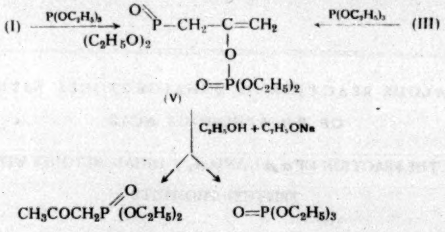
Reaction of triethyl phosphite with α, γ-dibromoacetone gave the 1-bromoisopropenyl-2-diethyl ester of phosphoric acid (III) (yield 40.2%). The normal product of reaction – phosphonobromoacetone – could not be isolated. After driving off about two-thirds of the reaction mixture, considerable resinification and decomposition of the residue was observed. When the reaction was carried out in ether solution at 20-25°, (III) was obtained as well as a very small residue. The structure of the 1-bromoisopropenyl-2-diethyl ester of phosphoric acid was confirmed by chlorination and ozonization. The products of these two reactions were respectively the 1-bromo-2,3-dichloroisopropyl-diethyl ester of phosphoric acid (IV) and formaldehyde. The latter was identified in the form of the products of condensation with β-naphthol and dimedon:



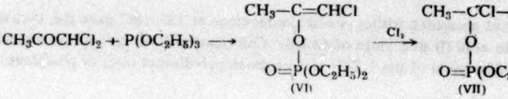
$$\mathrm{CH_2O \xleftarrow{O_3} BrCH_2{-}\underset{\substack{|\\ O\\ |\\ O{=}P(OC_2H_5)_2}}{C}{=}CH_2 \xrightarrow{Cl_2} BrCH_2{-}\underset{\substack{|\\ O\\ |\\ O{=}P(OC_2H_5)_2}}{CCl}{-}CH_2Cl}$$

(III) (IV)

When the reaction of α, γ-dibromoacetone with sodium diethyl phosphite was carried out, diphosphonacetone could not be isolated and a mixture of low-boiling products and undistillable residue was obtained. Further reactions of (I) and (III) with triethyl phosphite led to replacement of the halogen atom by the phosphono group and to formation of the (diethylphosphono-isopropenyl)-diethyl ester of phosphoric acid (V). The structure of (V) was confirmed by transesterification with ethyl alcohol in presence of a little sodium ethoxide. The resultant triethyl phosphate and diethyl phosphonacetone were identified through their constants:


(I)
$P(OC_2H_5)_3$
$(C_2H_5O)_2P(=O)-CH_2-C(=CH_2)-O-P(=O)(OC_2H_5)_2$
$P(OC_2H_5)_3$
(III)
(V)
$C_2H_5OH + C_2H_5ONa$
$CH_3COCH_2P(=O)(OC_2H_5)_2$
$O=P(OC_2H_5)_3$

The reaction between triethyl phosphite and α,α-dichloroacetone is extremely violent. Even when the reactants are brought into contact at room temperature, the temperature of the mixture gradually rises to 50°. The reaction then goes very quickly and the temperature rises violently to 110-120°; the reaction mixture boils up with evolution of much ethyl chloride. By cooling the reaction mixture with iced water, the reaction went at a lower and constant temperature (approx. 70°). Identical results are obtained in both cases. The 3-chloroisopropenyl-2-diethyl ester of phosphoric acid (VI) was isolated in 82.3% yield; no higher boiling products were detected. Chlorination of (VI) gave the 2,3,3-trichloroisopropyl-diethyl ester of phosphoric acid (VII):


$CH_3COCHCl_2 + P(OC_2H_5)_3$
$CH_3-C(=CHCl)-O-P(=O)(OC_2H_5)_2$
(VI)
Cl_2
$CH_3-CCl(-O-P(=O)(OC_2H_5)_2)-CHCl_2$
(VII)

The reaction of tri-n-butyl phosphite with α,α-dichloroacetone gives the 3-chloroisopropenyl-2-dibutyl ester of phosphoric acid in 76% yield. Similar reactions with α,α-dibromoacetone go less smoothly. Reaction of α,α-dibromoacetone with triethyl phosphite gave a 36.7% yield of the 3-bromoisopropenyl-2-diethyl ester of phosphoric acid. Its chlorination led to the 3-bromo-2,3-dichloroisopropyl ester of phosphoric acid.

EXPERIMENTAL

Reaction of triethyl phosphite with α, γ-dichloroacetone. To 31.3 g α, γ-dichloroacetone, heated to 120° in an Arbuzov flask, was added dropwise 40 g triethyl phosphite. The temperature of the reaction mixture was held at 125-130°. The reaction is exothermic. Ethyl chloride came off during the reaction. A series of fractionations of the reaction mixture from a flask with Widmer column gave 25.2 g of the 1-chloroisopropenyl-2-diethyl ester of phosphoric acid.

B. p. 133.5 - 134.5° at 11 mm, d_4^{20} 1.1934, n_D^{20} 1.4435, MR_D 50.81; calc. 50.91. Found %: Cl 15.60, 15.35; P 13.68. $C_7H_{14}O_4ClP$. Calculated %: Cl 15.54; P 13.57.

Analysis for double bond. 0.2900 g substance : found Br 0.1856 g; calculated Br 0.2030 g.

4,5 g of a higher boiling fraction was also obtained, and failed to yield a substance with constant boiling point.

Addition of chlorine to 1-chloroisopropenyl-2-diethyl ester of phosphoric acid. Chlorine was slowly passed through a solution of 5.5 g phosphoric ester in 30 ml carbon tetrachloride while cooling with a mixture of ice and salt. At first the solution remained colorless, but it acquired a permanent yellow color after the theoretical increase in weight (1.7 g). Fractionation of the reaction mixture gave 5.4 g 1,2,3-trichloroisopropyl-diethyl ester of phosphoric acid.

B.p. 150-152° at 9 mm, d_4^{20} 1.3593, n_D^{20} 1.4631, MR_D 60.70; calc. 61.12. Found %: Cl 36.09; P 10.53, 10.71. $C_7H_{14}O_4Cl_3P$. Calculated %: Cl 35.56; P 10.35.

Reaction of triethyl phosphite with α,γ-dibromoacetone. 63 g triethyl phosphite was added dropwise to 80.9 g α,γ-dibromoacetone heated to 120°. The temperature of the reaction mixture was held at 125-130°. 40 g ethyl bromide was distilled off. Fractionation of the reaction mass gave 42.4 g of the 1-bromoisopropenyl-2-diethyl ester of phosphoric acid.

B.p. 142.5 - 143° at 11 mm, d_4^{20} 1.3928, n_D^{20} 1.4622, MR_D 54.23; calc. 53.81. Found %: Br 29.32; P 11.56. $C_7H_{14}O_4BrP$. Calculated %: Br 29.31; P 11.36.

The residue (20-25 g) decomposed on fractionation. A second reaction of triethyl phosphite with α,γ-dibromoacetone carried out at a low temperature (20-25°), gave the 1-bromoisopropenyl-2-diethyl ester of phosphoric acid and only a very small quantity of residue.

Addition of chlorine to the 1-bromoisopropenyl-2-diethyl ester of phosphoric acid. Chlorination of 8.4 g of phosphoric ester was effected by the procedure described in the preceding experiment. 6.9 g of the 1-bromo-2,3-dichloroisopropyl-diethyl ester of phosphoric acid was obtained.

B.p. 159° at 9 mm, d_4^{20} 1.5163, n_D^{20} 1.4733, MR_D 63.66; calc. 64.01. Found %: Cl + Br 44.55; P 9.36, 9.32. $C_7H_{14}O_4PBrCl_2$. Calculated %: Cl + Br 43.9; P 9.01.

Ozonization of 1-bromoisopropenyl-2-diethyl ester of phosphoric acid. Ozonized oxygen (1-2% ozone) was passed for 14 hours into a solution of 4 g of the phosphoric ester in 20 ml dry carbon tetrachloride cooled with a mixture of ice and salt. After suction-filtering of the solvent in vacuum, the ozonides were decomposed with water while heating on a boiling water for 4 hours. From the distillate (which had a sharp formaldehyde odor) dinaphthylmethane was precipitated with the help of β-naphthol; the derivative, after recrystallization from aqueous alcohol, had m.p. 195-196° (in a mixed test the m.p. was 196-197°). A crystalline precipitate was obtained with dimedon; m.p. 189-190° after recrystallization. Mixed sample had m.p. 189°.

Reaction of 1-chloroisopropenyl-2-diethylphosphoric ester with triethyl phosphite. A mixture of 7.45 g phosphoric ester and 7 g triethyl phosphite was heated in a sealed tube at 240° for 4 hours. Fractionation of the reaction mixture gave 5.4 g of the 1-diethylphosphonisopropenyl-2-diethyl ester of phosphoric acid.

B.p. 193-195° at 9 mm, d_4^{20} 1.1623, n_D^{20} 1.4435, MR_D 75.34; calc. 75.38. Found %: P 18.84, 18.47. $C_{11}H_{24}O_7P_2$. Calculated %: P 18.79.

Reaction of the 1-bromoisopropenyl-2-diethyl ester of phosphoric acid with triethyl phosphite. A mixture of 8.1 g of the phosphoric ester and 12.3 g triethyl phosphite was refluxed in a flask at the boiling point of the reaction mixture for 5 hours. Fractionation of the reaction mixture gave 8.6 g of the 1-diethylphosphonisopropenyl-2-diethyl ester of phosphoric acid.

B.p. 195-197° at 10 mm, d_4^{20} 1.1645, n_D^{20} 1.4440, MR_D 75.27; calc. 75.38.

Reaction of triethyl phosphite with α,α-dichloroacetone. 25.2 g α,α-dichloroacetone was reacted with 33.2 g triethyl phosphite. A rise of temperature, at first slow, started 1-2 minutes after bringing the reactants into contact. When 50° was reached, further rise of temperature occurred violently to 110-120°. The mixture boiled up and much ethyl chloride was evolved. When the temperature of the reaction mixture started to fall, it was heated for ½ hour at 100-110°. Fractionation of the mixture from a flask with a Widmer column gave 37.3 g of the 3-chloroisopropenyl-2-diethyl ester of phosphoric acid.

B.p. 116.5-117° at 10 mm, d_4^{20} 1.1833, n_D^{20} 1.4370, MR_D 50.60; calc. 50.91. Found %: Cl 15.76; P 13.39, 13.63. $C_7H_{14}O_4ClP$. Calculated %: Cl 15.53; P 13.56.

Addition of chlorine to the 3-chloroisopropenyl-2-diethyl ester of phosphoric acid. A slow stream of chlorine was passed into a solution of 10 g of the phosphoric ester in 20 ml dry carbon tetrachloride until the weight increase was 3 g. The mixture turned yellow during chlorination; when the chlorine stream was stopped the liquid quickly became colorless. After absorption of the theoretical amount of chlorine (3 g), the reaction mixture acquired a stable yellowish-green color which only disappeared after prolonged standing at room temperature. Fractionation of the reaction mixture gave 9.6 g 1,2,3-trichloroisopropyl-diethyl ester of phosphoric acid.

B.p. 147 - 148° at 11 mm, d_4^{20} 1.3414, n_D^{20} 1.4580, MR_D 60.93; calc. 61.12. Found %: Cl 35.37, 35.69; P 10.31, 10.53. $C_7H_{14}O_4Cl_3P$. Calculated %: Cl 35.56; P 10.35.

Reaction of tri-n-butyl phosphite with α,α-dichloroacetone. On bringing 15 g tri-n-butyl phosphite into contact with 8 g α,α-dichloroacetone, the temperature rose to 50° in the course of a few minutes. The flask was later cooled with iced water and the temperature continued to rise to 90°. After brief heating on a water bath the reaction mixture was fractionated and gave 13.6 g of the 1-chloroisopropenyl-2-di-n-butyl ester of phosphoric acid.

B.p. 154-155° at 11 mm, d_4^{20} 1.0892, n_D^{20} 1.4400, MR_D 68.90; calc. 69.38. Found %: Cl 12.64; P 11.31. $C_{11}H_{22}O_4ClP$. Calculated %: Cl 12.47; P 10.89.

Transesterification of the 1-diethylphosphonisopropenyl-2-diethyl ester of phosphoric acid. 5.4 g of phosphoric ester was run into a solution of sodium ethoxide prepared from 0.2 g sodium and 15 ml anhydrous alcohol. The mixture was heated on a water bath for 30 minutes. Fractionation of the mixture from a flask with a Widmer column gave 0.7 g triethyl phosphate with b.p. 90-91° at 9 mm, n_D^{20} 1.4038, and 0.8 g phosphonacetone with b.p. 136-137° at 17 mm, n_D^{20} 1.4352. According to our previous paper [2], the latter has b.p. 126° at 9 mm, n_D^{20} 1.4350.

Reaction of α, γ-dibromoacetone with sodium diethyl phosphite. 30 g α, γ-dibromoacetone was added dropwise to 44.4 g ethereal solution of sodium diethyl phosphite prepared from 6.3 g sodium and 38.3 diethylphosphorous acid. The reaction mixture was centrifuged to separate the colloidal precipitate of sodium bromide. Fractionation of the reaction mixture gave: 1) fraction with b.p. 87-89° at 8 mm (9.5 g), d_4^{20} 1.0624, n_D^{20} 1.4060; 2) fraction with b.p. 117-127° at 9 mm (1.1 g), d_4^{20} 1.0914, n_D^{20} 1.4310. A Beilstein test for halogen in these fractions was negative; they were not further investigated. The residue resinified during fractionation.

Reaction of triethyl phosphite with α,α-dibromoacetone. To 25 g α,α-dibromoacetone, heated to 120°, was added dropwise 20 g triethyl phosphite. The temperature of the reaction mixture was held at 125-130°. Ethyl bromide came off during the reaction. Fractionation of the reaction mixture gave 11.6 g of the 3-bromoisopropenyl-2-diethyl ester of phosphoric acid.

B.p. 126-127° at 10 mm, d_4^{20} 1.3643, n_D^{20} 1.4540, MR_D 54.17; calc. 53.814. Found %: Br 29.64; P 11.35, 11.71. $C_7H_{14}O_4BrP$. Calculated %: Br 29.31; P 11.36.

Chlorination of 3-bromoisopropenyl-2-diethyl ester of phosphoric acid. Chlorination of 5.6 g of the phosphoric ester was effected by the method described above. Fractionation of the reaction mixture gave 2.8 g of the 1-bromo-1,2-dichloroisopropyl-diethyl ester of phosphoric acid.

B.p. 154-155° at 10 mm, d_4^{20} 1.4997, n_D^{20} 1.4735, MR_D 64.37; calc. 64.01. Found %: Cl + Br 45.06, 44.89; P 9.21, 9.32. $C_7H_{14}O_4Cl_2BrP$. Calculated %: Cl + Br 43.90; P 9.01.

SUMMARY

1. Reaction of α, γ-dichloro- and α, γ-dibromoacetone with triethyl phosphite led to 40-45% yields of the 1-chloro- and 1-bromoisopropenyl-2-diethyl esters of phosphoric acid. Their structure was verified by chlorination and ozonization reactions. Further reaction of both products with diethyl phosphite gave the 1-diethylphosphonisopropenyl-2-diethyl ester of phosphoric acid.

2. The reactions of triethyl phosphite with α,α-dichloro- and α,α-dibromoacetones proceed anomalously with formation of the 3-halodiisopropenyl-2-dialkyl esters of phosphoric acid.

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Received June 7, 1955

Kazan State University

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* T.p. = C. B. Translation pagination.

INVESTIGATIONS ON DERIVATIVES OF ALKYLPHOSPHINOUS AND DIALKYLPHOSPHINIC ACIDS

III. THE ATOMIC REFRACTION OF PHOSPHORUS IN ESTERS OF ALKYLPHOSPHINOUS ACIDS

A. Razumov and O. Mukhacheva

The atomic refraction of phosphorus in organic compounds is extremely sensitive to structural factors and depends on the valence state of the phosphorus and on the character of the bonds. It has been repeatedly calculated by various authors over a period of over 50 years on a very large number of compounds [1-7].

The values of the atomic refraction of phosphorus in esters of phosphorous acid and in phosphines, in which phosphorus is trivalent, and in esters of phosphoric and alkylphosphinic acids, in which the element is pentavalent, can be considered reliable (Table 1).

TABLE 1

The Atomic Refraction of Phosphorus

Types of compounds	Valency of phosphorus	Atomic refraction of phosphorus	Literature
$(RO)_3P{=}O$	5	3.75	[3]
$(RO)_2\underset{\overset{\Vert}{O}}{P}—R$	5	4.27	[7]
$(RO)_3P$	3	7.04	
$(R)_3P$	3	9.14	[6

Two conclusions can be drawn from Table 1: 1) The view of A. E. Arbuzov and A. A. Ivanov [3] that the atomic refraction of phosphorus is greatly influenced by structural factors and that the refraction is higher in trivalent than pentavalent compounds is undoubtedly correct, since it has been confirmed in our day on a large number of compounds. 2) In our own opinion, a law is manifested in organic compounds of phosphorus, characterized by an increase in the value of the atomic refraction of phosphorus with each substitution of an OR group by R. This law is illustrated by the compounds discussed below.

This regularity first attracted our attention when calculating the molecular refraction of esters of dialkylphosphinic acids with application of 4.27 as the atomic refraction of P, reliably calculated by M. I. Kabachnik for the alkylphosphinic acids [7]. This value proved unsuitable for esters of dialkylphosphinic acids. Good results were only obtained when this value was increased by approximately 0.5, i.e. by the difference between the value of the atomic refraction of phosphorus in esters of alkylphosphinic acids and that in esters of phosphoric acid (4.27 - 3.75 = 0.52). The same difficulties were encountered by G. Kosolapoff [8] in the same year and led to similar conclusions. He proposed a value of 4.79 for the atomic refraction of phosphorus in esters of dialkylphosphinic acids. Although the value proposed by G. Kosolapoff was calculated only on the basis of two compounds, it can nevertheless be considered corret, because we checked it on a large number of compounds and also because it was later calculated by M. I. Kabachnik and E. S. Shepeleva who obtained a value of 4.85 [9]. Consequently, in the light of the facts given above we can say that in full alkyl esters in which phosphorus is pentavalent, the atomic refraction of P increases with each replacement of OR by R, the magnitude of the increase being 0.5 as pointed out by G. Kosolapoff [8].

In our later investigations we encountered exactly the same difficulty in calculating the molecular refraction of esters of alkylphosphinous acids on the assumption that the atomic refraction of P is 7.04 (as accepted for esters of phosphorous acid). For this reason we prepared 6 representatives of these compounds in large amounts, which allowed us to purify them thoroughly, and we calculated the atomic refraction of the phosphorus in them (Table 2).

As we see, if we ignore Compound 5 (which was not amenable to thorough purification) we obtain a mean value of ARp = 7.80 with maximum deviations of +0.11 and −0.15.

TABLE 2

№	Formula of compound	d_4^{20}	n_D^{20}	MR_D	Atomic refraction of phosphorus AR_P
1	$C_2H_5P(OC_2H_5)_2$	0.9063	1.4222	42.12	7.83
2	n-$C_3H_7P(OC_2H_5)_2$	0.9029	1.4275	46.73	7.82
3	n-$C_3H_7P(OC_3H_7)_2$	0.8917	1.4223	55.95	7.80
4	n-$C_4H_9P(OC_2H_5)_2$	0.8963	1.4308	51.44	7.91
5	n-$C_4H_9P(OC_3H_7)_2$	0.8961	1.4355	60.12	7.35
6	n-$C_4H_9P(OC_4H_9)_2$	0.8883	1.4410	69.65	7.65

On the basis of the results that we obtained, we can conclude that for calculation of the atomic refraction in esters of alkylphosphinous acids it is impossible to use the value of AR_P = 7.04 accepted for phosphites.

We therefore advanced the hypothesis that both in compounds of trivalent phosphorus and of pentavalent phosphorus the value of AR_P rises with replacement of each OR group by R. In this manner we obtain the following series of compounds with increasing atomic refraction of phosphorus:

$$(RO)_3P < RP(OR)_2 < R_2P(OR) < R_3P.$$

Since the value of the atomic refraction of phosphorus is known for phosphites (7.04) [7] and for phosphines (9.14) [5,6], determination of the difference between individual values on substitution of each OR group by R leads to a value of 0.7; it follows that for esters of alkylphosphinous acids the atomic refraction of phosphorus must be equal to 7.74, while for esters of dialkylphosphinous acids it must be equal to 8.44. The former value of 7.74 is in good agreement with the mean value of 7.80 calculated for the esters that we synthesized.

With an atomic refraction of phosphorus equal to 7.74, the agreement between the experimental and calculated MR_D for the esters of alkylphosphinous acids that we synthesized is very good (Table 3).

TABLE 3

Comparison of Experimental and Calculated Molecular Refraction

Formula	Found	Calculated
$C_2H_5P(OC_2H_5)_2$	42.12	42.03
n -$C_3H_7P(OC_2H_5)_2$	46.73	46.65
n -$C_3H_7P(OC_3H_7)_2$	55.95	55.88
n -$C_4H_9P(OC_2H_5)_2$	51.44	51.27
n -$C_4H_9P(OC_4H_9)_2$	69.65	69.74

For esters of dialkylphosphinous acids our proposed value of AR_P of 8.44 is in good agreement with the values calculated for a series of esters of diethylphosphinous acid synthesized by B. A. Arbuzov and N. I. Rizpolozhensky [12] (Table 4).

The mean value of AR_P is 8.42 with maximum deviations of +0.30 and -0.23. This value is in adequate agreement with that proposed by us (8.44).

The observed regularity of change of AR_P with substitution of the OR group by R in alkyl esters of various acids of phosphorus and of phosphines is shown in generalized form in Table 5.

TABLE 4

Atomic Refraction of Phosphorus in Esters of Diethylphosphinous Acid .

Formula	d_4^{20}	n_D^{20}	MR_D calc.	AR_P
$(C_2H_5)_2POC_2H_5$	0.8496	1.4328	41.03	8.38
$(C_2H_5)_2POC_3H_7$- n	0.8523	1.4365	45.50	8.23
$(C_2H_5)_2POC_3H_7$- iso	0.8395	1.4320	45.70	8.41
$(C_2H_5)_2POC_4H_9$- n	0.8516	1.4410	50.32	8.43
$(C_2H_5)_2POC_4H_9$- iso	0.8430	1.4381	50.55	8.66
$(C_2H_5)_2POC_6H_{13}$n	0.8503	1.4448	59.55	8.73
$(C_2H_5)_2POC_7H_{15}$n	0.8547	1.4495	64.18	8.44
$(C_2H_5)_2POC_8H_{17}$n	0.8579	1.4520	68.65	8.29
$(C_2H_5)_2POC_9H_{19}$n	0.8584	1.4525	73.18	8.20
$(C_2H_5)_2POC_{10}H_{21}$n	0.8531	1.4531	78.09	8.49

TABLE 5

Change of Atomic Refraction of Phosphorus on Replacement of the OR Group by R

Type of Compound	Valence	Value of AR_P		Literature
$RO)_3P{=}O$	5	3.75	0.52	[3]
$(RO)_2P(O)R$	5	4.27		[7]
$ROP(O)R_2$	5	4.79	0.52	[8]
$(RO)_3P$	3	7.04	0.7	[7]
$(RO)_2PR$	3	7.74		Our data
$ROPR_2$	3	8.44	0.7	Our data
PR_3	3	9.14	0.7	[5,6]

In 1952 accounts were published of the synthesis and some properties of esters of ethyl- and isobutylphosphinous acids [10, 11]. In the present paper we describe the synthesis and present the constants of the following homologs: esters of n-propylphosphinous and n-butylphosphinous acids.

All the esters were prepared by the action of the corresponding dichlorophosphines in ethereal solution upon a mixture of the alcohol and pyridine.

$$RPCl_2 + 2ROH + 2C_5H_5N \longrightarrow RP(OR)_2 + 2C_5H_5N \cdot HCl.$$

The most important factor in the synthesis is the protection of the esters from atmospheric oxygen, since they are easily oxidized. All the operations of the synthesis (filtration, fractional distillation, etc.) were therefore performed in an atmosphere of nitrogen or carbon dioxide. The starting dichlorophosphines were brought into reaction in quite large amounts (up to 250 g). This permitted thorough fractional distillation of the esters in an efficient column and their separation from possible oxidation products.

The process of synthesis itself was carried out at near 0°, only the completion of the reaction being effected by heating for 30-40 minutes to the boiling point of the solvent.

Yields of esters, boiling points and analyses are set forth in Table 6.

TABLE 6

Formula	Boiling point	Pressure (in mm)	Phosphorus content calculated	Phosphorus content found	Yield (in %)
n $-C_3H_7P(OC_2H_5)_2$	52—53°	12	18.90	18.75, 18.78	64
n $-C_3H_7P(OC_3H_7)_2$	81—82	11	16.14	16.15, 15.95	74
n $-C_4H_9P(OC_2H_5)_2$	68.5—70	12	17.41	17.49, 17.62	64
n $-C_4H_9P(OC_3H_7)_2$	99.5—101	14	15.04	15.06, 15.09	60
n $-C_4H_9P(OC_4H_9)_2$	116.5—118	10	13.25	13.41, 13.40	64

The specific gravity and refractive index of the synthesized esters are given in Table 3 and the values of MR_D found are given in Table 4. The esters are colorless liquids with an unpleasant odor of mixed phosphines and phosphites. They have good solubility in a wide variety of organic solvents.

SUMMARY

1. Esters of n-propyl- and n-butylphosphinous acids were synthesized.

2. A regularity of change of atomic refraction of phosphorus on transition of the alkyl esters with trivalent phosphorus to phosphines was found. Each substitution of an OR group by R causes an increase of 0.7 in the atomic refraction of phosphorus.

3. The atomic refraction of phosphorus in esters of alkylphosphinous acids can be assumed equal to 7.74, and that in esters of dialkylphosphinous acids to 8.44.

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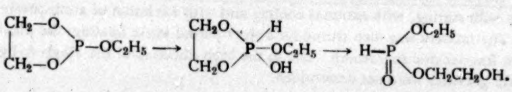
Received September 19, 1955

S. M. Kirov Institute of Chemical
Technology, Kazan

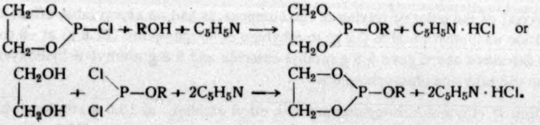
PREPARATION OF SOME ALKYL-β-HYDROXYETHYLPHOSPHOROUS ACIDS

E. L. Gefter

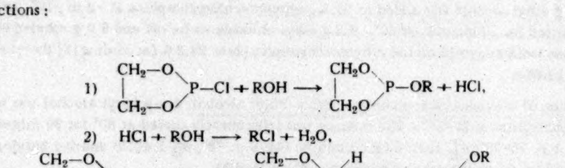
Alkyl-β-hydroxyethylphosphorous acids of the general formula (I) have scarcely been studied. The only representative of this class of substances that has been described is ethyl-β-hydroxyethylphosphorous acid, which was obtained by A. E. Arbuzov and co-workers [1] by treatment of the ethyl ester of ethylene glycol phosphorous acid with water:



The starting substances for the preparation of alkyl-β-hydroxyethylphosphorous acids are esters of ethylene glycol phosphorous acid which were synthesized by reaction of ethylene chlorophosphite with alcohols, or by reaction of Menshutkin acid chlorides with glycols in presence of organic bases [1-3]:



In investigating the reaction of ethylene chlorophosphite with anhydrous alcohols in the absence of organic bases, we succeeded in showing that some of the reaction products (in the case of lower alcohols) are alkyl-β-hydroxyethylphosphorous acids of the general formula (I). It may be suggested that the latter are formed by the following reactions:



(alkyl chlorides, which are obtained according to the above scheme, were isolated). The yield of alkyl-β-hydroxyethylphosphorous acids fell rapidly with increasing molecular weight of the alcohol used.

Alkyl-β-hydroxyethylphosphorous acids are transparent, colorless, extremely viscous and nearly odorless liquids, distilling in vacuum without decomposition.

EXPERIMENTAL

Preparation of ethylene chlorophosphite (freshly distilled reactants and solvent were used). 288 g phosphorus trichloride and 10 ml chloroform were placed in a four-necked flask fitted with dropping funnel, reflux condenser closed with calcium chloride tubes, a thermometer and a stirrer. A mixture of 130 g ethylene glycol and 200 ml chloroform was added over a period of 20-30 minutes with good stirring. Hydrochloric acid came off vigorously and the temperature of the reaction mixture gradually fell to 6-8° without external cooling. The contents of the flask were then heated to 30°; the chloroform was at once distilled off at 120-140 mm to a bath temperature of 50°, while the reaction product was distilled at 12-13 mm to a bath temperature of 100°. A redistillation gave pure ethylene chlorophosphite. Yield 192 g (72.5%). The product is a colorless transparent liquid, fuming in the air.

B.p. 53-54° at 22-23 mm, d_4^{20} 1.4178, n_D^{20} 1.4910, MR_D 25.85; calc. 25.90. Literature data [1]: b.p. 41.5 at 10 mm, d_4^{20} 1.4172, n_D^{20} 1.4915.

Reaction of ethylene chlorophosphite with anhydrous alcohols. In all cases one component was added to the other dropwise with stirring, with external cooling and with exclusion of atomspheric moisture from the reaction system. The mixture was then stirred for a short period while heating; the alkyl halide was distilled off and the residue fractionated in vacuum. Due to the high viscosity of the alkyl-β-hydroxyethylphosphorous acids, their specific gravities were not determined.

1) Reaction of ethylene chlorophosphite with methyl alcohol. a) To 10 g methyl alcohol was added 19.4 g ethylene chlorophosphite at 0°. Stirring was later carried out at 50-55° for 1 hour. 5.1 g halogen-containing liquid (Beilstein test) was condensed in a trap cooled with solid carbon dioxide. The liquid burnt with a greenish flame and boiled at -23° (methyl chloride has b.p. -24°). The residue after distillation of the easily volatile fraction gave 10 g of very viscous, colorless, transparent liquid, free from chlorine and corresponding in phosphorus content to methyl-β-hydroxyethylphosphorous acid. Yield 46.5% on the ethylene chlorophosphite.

B.p. 128-129° at 1.5-2 mm, n_D^{20} 1.4762. Found %: P 21.98. $C_3H_9O_4P$. Calculated %: P 22.14.

b) A reversal of the order of mixing of the components had no appreciable effect on the reaction course. Thus, the addition of methyl alcohol (12 g) to ethylene chlorophosphite (21.6 g) at -8 to -10° followed by working up as described above gave 5.3 g methyl chloride and 9.2 g methyl-β-hydroxyethylphosphorous acid. Yield 38.5% on the ethylene chlorophosphite.

2) Reaction of ethylene chlorophosphite with ethyl alcohol. a) 13.5 g ethylene chlorophosphite was added to 8.3 g ethyl alcohol at 15-20°. Subsequent stirring was effected at 60° for 30 minutes. 4.8 g ethyl chloride with b.p. 10-12° was isolated (b.p. according to [4] 12.2°), in addition to 4.2 g ethyl-β-hydroxyethylphosphorous acid. Yield on the ethylene chlorophosphite 25.6%.

B.p. 133-135° at 2-2.5 mm, n_D^{20} 1.4852. Found %: P 20.01. $C_4H_{11}O_4P$. Calculated %: P 20.12.

b) 11.9 g ethyl alcohol was added to 20.3 g ethylenechlorophosphite at -8 to -10°, and the mixture was subsequently stirred for 30 minutes at 60°. 6.2 g ethyl chloride came off and 6.0 g ethyl-β-hydroxyethylphosphorous acid was isolated; yield on the ethylenechlorophosphite 24.3% (according [1] the yield on ethylenechlorophosphite is 19.6%).

3) Reaction of ethylenechlorophosphite with n-butyl alcohol. 8.1 g butyl alcohol was added to 11.3 g ethylenechlorophosphite at 20-25°. The mixture was subsequently stirred at 60° for 30 minutes. 5 g chloride came off with b.p. 76-78°, n_D^{20} 1.4018 (according to [4]: b.p. 78°, n_D^{20} 1.4015) and 2 g butyl-β-hydroxyethylphosphorous acid (yield on the ethylenechlorophosphite 12.3%).

B.p. 140-142° at 3-4 mm, n_D^{20} 1.4784. Found %: P 16.86. $C_6H_{15}O_4P$. Calculated %: P 17.03.

SUMMARY

1. A simplified synthesis of alkyl-β-hydroxyethylphosphorous acids is described; it involves reaction of ethylenechlorophosphite with anhydrous alcohols followed by fractionation of the reaction mixture.

2. Preparation were carried out by this method of ethyl-β-hydroxyethylphosphorous acid and of the previously undescribed methyl- and n-butyl- β-hydroxyethylphosphorous acids.

3. A mechanism of the formation of alkyl-β-hydroxyethylphosphorous acids is proposed.

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Received June 13, 1955

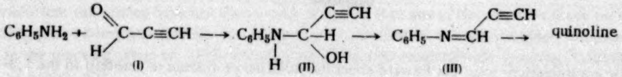
Institute of Plastics Research, Moscow

THE STRUCTURE OF THE PRODUCT OF REACTION OF ANILINE WITH PROPARGYL ALDEHYDE

I. Ya. Postovsky, R. O. Matevosyan and Yu. N. Sheinker

Claisen [1] reacted propargyl aldehyde (I) with aniline and obtained a substance with m.p. 122-123° which he regarded as the addition product (II). We established that products of addition are also obtained by action of propargyl aldehyde with other aromatic primary amines. Thus, for example, propargyl aldehyde reacts smoothyl with o-anisidine and with β-naphthylamine to give light-yellow crystalline substances. All the addition products break down to the original components on heating with dilute caustic alkalies and mineral acids.

In his paper Claisen does not present any data or put forward any ideas about the dehydration of the addition product (II) to the anil (III) and about the cyclization of the latter to quinoline:



The later literature likewise does not contain any information about the dehydration of the Claisen compound.

We attempted to effect the dehydration of this compound by heating with phosphorus pentoxide in benzene solution, and also by heating with zinc chloride, but these attempts did not lead to the desired result.* Only by heating with strong sulfuric acid at 60° could dehydration and ring closure be realized, although the yield of quinoline was small and amounted to only 9-15% in different experiments. The substance with structure (II) was expected to be easily dehydrated to the anil (III), but in spite of all efforts we were unable to raise the yield of quinoline to above 15%.** This behavior led us to doubt the correctness of formula (II) for the Claisen compound.

A compound with structure (II) ought to form acetylides with facility. In actual fact, it does not form a precipitate with ammoniacal silver nitrate solution, i.e. it does not give the reaction for methine hydrogen, whereas propargyl aldehyde itself immediately forms an acetylide under the same conditions. For this reason we concluded that addition of aniline to propargyl aldehyde does not proceed at all at the carbonyl, as was suggested by Claisen, but at the triple bond (addition in the 1,2- position) or possibly at the carbonyl and methine carbon of the aldehyde (addition in the 1,4- position). Various tautomeric compounds could be obtained in the event of 1,2- addition: β-anilinoacrolein (IV), the isomeric anil of malonaldehyde (V), and the tautomeric enol (VI). Addition in the 1,4- position ought to give the enol-allene (VII) which in turn could isomerize to one of the compounds mentioned. A compound with any of the structures (IV,V,VI or VII) could lead to quinoline.

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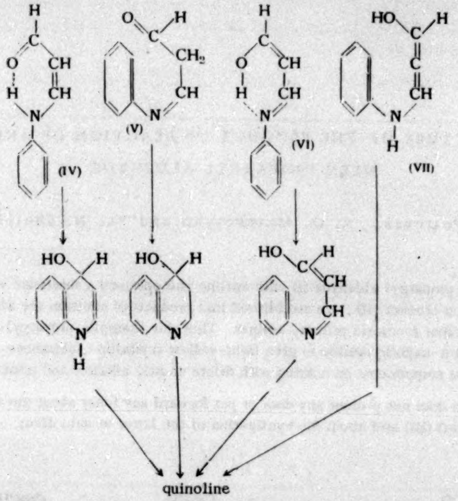
* The first experiments along these lines were undertaken by one of us in collaboration with M. A. Belous in 1950, but were interrupted by the death of the latter.

** Approximately the same low yield of quinoline is obtained in the analogous reaction of aniline with acrolein in presence of strong sulfuric acid and nitrobezene [2].



Similar considerations were put forward about the addition of aniline to acrolein in the 1,2- or the 1,4-position in connection with the mechanism of the Skraup reaction [2]. As we know, an intermediate product could not be isolated in this reaction, due to which the mechanism of the reaction of formation of quinoline from aniline and acrolein is still controversial [3]. In the reaction of aniline with propargyl aldehyde, however, the intermediate addition product (the Claisen compound) is stable and it would therefore seem possible to determine its structure and in turn to clarify the mechanism of its conversion to quinoline.

On steric grounds the closure to form a heterocycle should proceed most smoothly in the case of the aldehydic structure (V). Formation of a heterocycle from compounds (IV) and (VI) must be preceded by closure to a ring with a hydrogen bond followed by rotation of the side chain. It may be suggested that the most stable "hydrogen ring" would result from structure (VI) in which, in contrast to (V), the side chain is conjugated with the ring and, as is evident from a model, is in the same plane as the ring.*

An experimental check showed that the Claisen compound does not give reactions for the aldehyde group. Thus, fuchsinesulfurous acid does not change color, and no reactions take place with semicarbazide or with thiosemicarbazide. Heating with hydroxylamine hydrochloride in an alcoholic medium gives a hydrochloride with m.p. 212-213°, which is converted into a base with m.p. 112-113°. This substance was identified as the dianil of malonaldehyde (VIII). It is also formed without participation of hydroxylamine, simply by heating the Claisen compound with a little hydrochloric acid in an alcoholic medium. The same dianil had also been obtained from propargyl acetal and aniline hydrochloride [1]. The dianil was subsequently described several times in the literature [4-6], and its structure is not in doubt.

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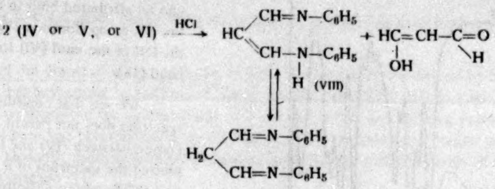
* The distance between the oxygen atom and the nitrogen atom in (VI) is smaller than in (IV), due to which the hydrogen bond in (VI) is more stable than in (IV). Due to the linear arrangement of the carbon atoms of the side chain in (VII), the corresponding distance is greater than 4 A, i.e. a hydrogen bond is here excluded.

The dianil (VIII) can evidently be equally formed from the aldehydes (IV, V) and from the enol (VI). Its formation can be represented by the following scheme.*



While not manifesting the properties of an aldehyde, the Claisen compound has an enolic reaction (the alcoholic solution colors FeCl$_3$ cherry-red).** The substance also gives this reaction in the crystalline state. Thus, if small crystals of the compound are rubbed on a filter paper previously moistened with FeCl$_3$ solution and then thoroughly dried, a violet-grey stain quickly develops below and around the crystals.

All these reactions are inconsistent with the aldehyde structure of (IV) and (V) and more consistent with formulas (VI) or (VII). It is impossible, however, to be certain that the enol reaction could not have developed during the reaction also as a result of isomerization of the aldehyde (IV or V) to the enol (VI), while the absence of an aldehyde reaction could be the consequence of masking of the carbonyl group by the hydrogen bond of (V) [9].

It is obvious that the choice between the isomers (IV), (V), (VI) and (VII) cannot be made on the basis of chemical investigation alone; we decided, therefore, to apply the method of infra-red absorption, since this permits the detection in the reacting substance of the presence or absence of characteristic groupings (allenic, carbonyl), bonds (double or triple), etc.

An absorption band was not detected in the absorption spectrum of the Claisen compound, plotted for the crystalline substance in suspension in vaseline oil, in the wide interval of 2500-1700 cm^{-1} (the triple bond region) (see diagram, Curve I). Consequently in the crystalline state it does not possess the enol-allene structure of (VII), for in this event an absorption band should have appeared in the 1980.1920 cm^{-1} region due to the asymmetrical vibration of the allene group [13].***

The absence of absorption bands in the 2200-2000cm^{-1} region, corresponding to the vibration of the triple bond [13,14], also supports the conclusion, arrived at in the chemical investigation, that the Claisen formula (II) is incorrect. Evidence against the acetylenic (II) and allenic (VII) formulas is the absence of absorption bands in the 3650-3400 cm^{-1} region where vibrations of "free" hydroxyl groups are manifested, i.e. hydroxyl not participating in the hydrogen bond; such hydroxyls appear in formulas (II) and (VII). Consequently we are left only with formulas (IV), (V) and (VI) for consideration of the structure of the Claisen compound.

A formula with the structure of (V) can be excluded in view of the absence of absorption bands in the 1760-1710 cm^{-1} region (region of valence vibration of "free" carbonyl) and in the 1460-1420 cm^{-1} region corresponding to the valence vibration of the methylene group. We are thus left with a choice between formulas (IV) and (VI).

The spectrum of the Claisen compound (diagram, Curve I) contains an intense absorption band at 1657 cm^{-1} (A). Its interpretation meets with difficulty since it can be correlated with the vibration of the carbonyl conjugated with the double bond and participating in the hydrogen bond (formula IV) and can also be correlated with the vibration of the C=N group (formula VI). Another band at 1623 cm^{-1} (B) can be reliably attributed to the vibration of the C=C group, but this group is present both in formula (IV) and formula (VI). The 1590 cm^{-1} band (C) is evidently associated with the vibrations of the phenyl. The 3220 and 3124 cm^{-1} bands present in the high-frequency portion of the spectrum can be attributed both to the valence vibration of the NH group (formula IV) and to the vibration of the OH of the enol (VI) linked by a strong hydrogen bond [15].

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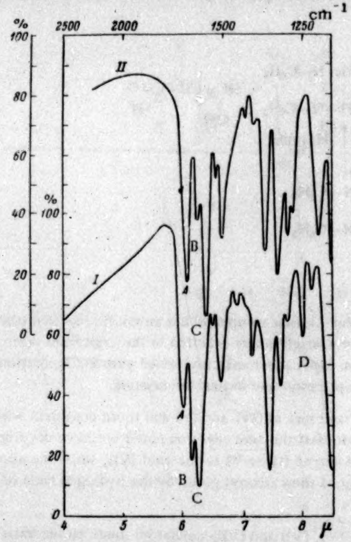
* A similar transformation has been described for the monoanil of chloromalonaldehyde [7].

** Wille and Saffer [8] likewise point out the ability of the Claisen compound to give the enol reaction. These authors propose, without any experimental support, the allene structure (VII) for the Claisen compound. No data for the Claisen compound are mentioned in the abstract of the paper.

*** Correlation of the absorption bands found with individual groups was based on tabulated data [10,11,12] and on a series of original papers cited in the text.

We see that consideration of the infrared spectrum does not permit us to make a definite choice between (IV) and (VI). For this reason we plotted the spectrum of a related compound, the anil (VIII), which definitely does not contain an aldehyde group but does contain the azomethine group C=N (diagram, Curve II).

The curve of the anil closely follows that of the curve of the spectrum of the Claisen compound. The spectrum of the dianil contains a strong band at 1645 cm^{-1} (A) whose position nearly coincides with that of 1650 cm^{-1} band (A) in the spectrum of the Claisen compound. The 1645 cm^{-1} band can only be associated with the C=N group; consequently, the 1650 cm^{-1} band in the lower curve must likewise be attributed to the vibration of the C=N group. The spectrum of the Claisen compound contains a strong absorption band at 1240 cm^{-1} (D) which is absent from the dianil spectrum. It must be clearly attributed to the deformation vibration of the hydroxyl or of the C-O group. *



Infrared absorption spectra.
I) Claisen compound; II) dianil of malonaldehyde.

On the basis of the chemical properties of the Claisen compound and in particular of the infrared absorption spectra of this compound, it can be considered highly probable that the product of addition of aniline to propargyl aldehyde has the structure of the anil of malonaldehyde in the enol form, stabilized by a hydrogen bond (VI). Reaction of aniline with propargyl aldehyde evidently results initially in addition in the 1,4- position and formation of the unstable allene (VII), which becomes stabilized on isomerization to the enol (VI). The chemical data set forth above are also consistent with formula (VI) – the sensitivity to alkalies and acids, the definite enolic reaction, and the absence of aldehydic properties.

EXPERIMENTAL

1. Preparation of the anil of malonaldehyde in the enolic form (Claisen compound) (VI). A mixture of 6 g (0.1 mole) freshly distilled propargyl aldehyde (b.p. 59-60°) and 10 ml benzene was gradually run into a mixture of 10 g (0.1 mole) aniline and 20 ml benzene cooled with ice. The light-yellow precipitate was collected and washed with benzene. M.p. 122-123° (from benzene) (literature 122-123°). Uniform, light-yellow prisms. Yield 12.2 g (77%).

Found %: C 73.66; H 6.05; N 9.21. C_9H_9ON. Calculated %: C 73.40; H 6.12; N 9.50.

2. Preparation of products of reaction of propargyl aldehyde with o-anisidine and β-naphthylamine. Reaction of o-anisidine with propargyl aldehyde in benzene solution gave a 60% yield of addition product in the form of light-yellow needles with m.p. 112-114° (from benzene).

Found %: N 8.07. $C_{10}H_{11}O_2N$. Calculated %: N 7.89.

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* The 1235 cm^{-1} band in phenol, for example, is attributed to the deformation vibration of the OH group [16]. The 1220 cm^{-1} band has been frequently attributed to the C-O group [17].

Similarly, β-napthylamine gave a 79% yield of addition product in the form of light-yellow elongated needles with m.p. 124-125° (from benzene).

Found %: N 7.28 . $C_{13}H_{14}ON$. Calculated %: N 7.15.

Products similar to the Claisen compound gave an enolic reaction and must have a structure analogous to (VI).

3. Formation of the dianil of malonaldehyde. (VIII). a) The dianil was formed by heating the Claisen compound (6 g) with hydroxylamine hydrochloride (2.8 g) in 70% alcohol (30 ml) on a water bath for 3 hours. On cooling, the solution deposited the hydrochloride of the dianil in the form of long yellow needles with m.p. 212-213°. The dianil base was precipitated from the filtrate by dilute ammonia. Light-yellow needles with m.p. 114-115° (from alcohol), melting without depression in admixture with the dianil of malonaldehyde prepared by Claisen's method [1].

b) The dianil was also obtained by heating the Claisen compound (2 g) in a solution of 30% alcohol (20 ml),to which had been added a small amount of 2 N hydrochloric acid (5 ml), on a water bath for 3 hours. The reaction products were worked up as in the preceding experiment. Yield of dianil (base) 1.1 g (82%), m.p. 114-115°.

4. Preparation of quinoline from Claisen compound (VI). 60 g compound (VI) was gradually stirred into 160 ml strong sulfuric acid. After heating of the mixture on a water bath at 55-60° for 3 hours, the viscous dark-cherry solution was poured into 800 ml water. The solution was made alkaline with 30% sodium hydroxide and the quinoline was distilled off with steam. The quinoline was freed from traces of aniline in the usual manner [18]. Yield 4.9 g quinoline (9%), b.p. 226-229° (739 mm). Picrate m.p. 202°, n_D^{20} 1.6180.

5. Absorption spectra. Infrared spectra were obtained with the help of the IKS-11 recording infrared spectrometer (NaCl prism for the 5.5-14μ region and LiF prism for the 1.5-5.5μ region). Compounds (VI) and (VIII) were plotted in the crystalline state in suspension in vaseline oil.

Absorption bands of compound (VI). LiF prism: 3230, 3124, 3075, 3080, 2950, 2810, 2755.

NaCl prism: 1650, 1620, 1590, 1503, 1393, 1340, 1308, 1288, 1245, 1218, 1182, 1031, 988, 881, 858, 842, 827, 754, 722 cm^{-1}.

Absorption bands of compound (VIII). NaCl prism: 1645, 1590, 1565, 1504, 1359, 1318, 1290, 1276, 1212, 1185^{-1}.

SUMMARY

1. On the basis of chemical investigation and of infrared absorption measurements, it is concluded that the product of addition of aniline to propargyl aldehyde does not possess the structure of N-(α-hydroxypropargyl)-aniline assigned to it by Claisen.

2. The most probable structure of the Claisen compound is (VI) -- the anil of malonaldehyde in the enolic form strengthened by a hydrogen bond.

3. Heating of the anil (VI) with strong sulfuric acid gives quinoline in 9-15% yield.

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Received June 9, 1955

Ural Polytechnic Institute

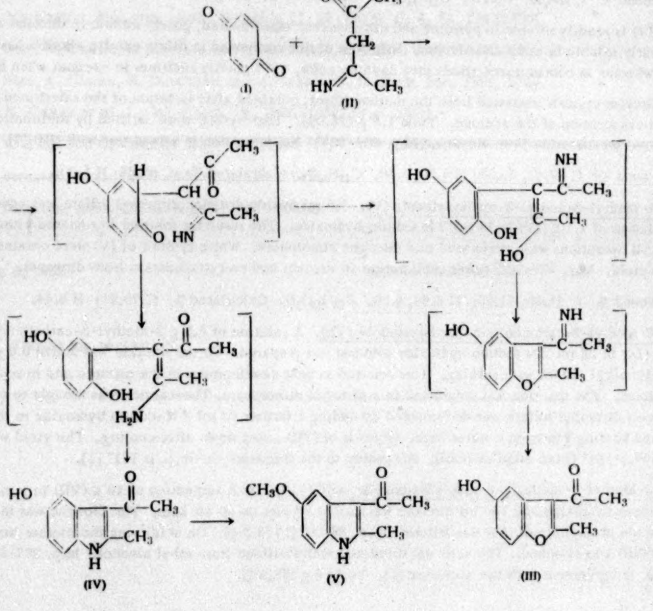
INVESTIGATIONS ON QUINONES

X. REACTION OF ACETYLACETONIMINE WITH p-QUINONE

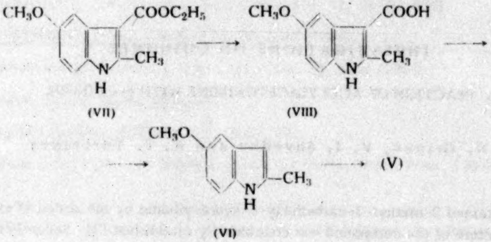
A. N. Grinev, V. I. Shvedov and A. P. Terentyev

Nenitzescu [1] obtained 2-methyl-3-carbethoxy-5-hydroxyindole by the action of ethyl β-aminocrotonate on p-quinone. The structure of the compound was conclusively established [2]. Recently the reaction of ethyl β-aminocrotonate and its nearest analogs with some p-quinones has led to the synthesis of a series of other substituted indoles [3,4].

In the present work we have made a study for the first time of the reaction of p-quinone (I) with acetylacetonimine (II), obtained by the action of ammonia on acetylacetone [5]. We were able to establish that this reaction leads to the known 2-methyl-3-acetyl-5-hydroxybenzofuran (III) [6,7] and 2-methyl-3-acetyl-5-hydroxyindole (IV):



The structure of (IV) was confirmed by transformation into 2-methyl-3-acetyl-5-methoxyindole (V). We also synthesized the latter by acylation of 2-methyl-5-methoxyindole (VI). During the synthesis of (VI) improvements were effected in the procedure for hydrolysis of 2-methyl-3-carbethoxy-5-methoxyindole (VII) and of decarboxylation of 2-methyl-5-methoxy-3-indolyl-carboxylic acid (VIII), which enabled (VI) to be obtained in good yield.



EXPERIMENTAL

Condensation of p-quinone with acetylacetonimine. A solution of 2.8 g of the imine in 8 ml acetone was added to a solution of 3 g p-quinone in 8 ml dry acetone. The reaction mixture was heated one hour on a water bath. The precipitate coming down from the cooled solution was separated and washed with ether. Yield of (IV) 2 g (38.1%). After two recrystallizations from pyridine white crystals with m.p. 292-293° were obtained.

Found %: C 69.26; H 5.79. $C_{11}H_{11}O_2N$. Calculated %: C 69.82; H 5.86.

(IV) is readily soluble in pyridine and nitrobenzene when heated, poorly soluble in dioxane and acetone, very poorly soluble in ether and alcohol. Solutions of this compound in dilute caustic alkalies have a cherry-red color, whereas in concentrated alkali they have no color. (IV) readily sublimes in vacuum when heated.

Greyish crystals separated from the mother liquor, obtained after isolation of the substituted indole, on gradual evaporation of the acetone. Yield 1.5 g (28.9%). The crystals were purified by sublimation in vacuum and by recrystallization from dioxane. M.p. 234-235°. No depression in mixed test with (III) [7].

Found %: C 69.47, 69.50; H 5.50, 5.49. $C_{11}H_{10}O_3$. Calculated %: C 69.46; H 5.30.

2-Methyl-3-acetyl-5-methoxyindole (V). 1.5 ml freshly distilled dimethyl sulfate was added with stirring to a solution of 1.1 g (IV) in 15 ml 2 N sodium hydroxide. The resultant solution was heated $\frac{1}{2}$ hour on a water bath. All operations were performed in a nitrogen atmosphere. White crystals of (V) were obtained in quantitative yield. M.p. 227-228° (after sublimation in vacuum and recrystallization from dioxane).

Found %: C 71.39, 71.25; H 6.69, 6.50. $C_{12}H_{13}O_2N$. Calculated %: C 70.91; H 6.44.

2-Methyl-3-carbethoxy-5-methoxyindole (VII). A solution of 5.5 g 2-methyl-3-carbethoxy-5-hydroxyindole (IX) in 36 ml 2 N sodium hydroxide solution was prepared. To the solution was added 6.6 g freshly distilled dimethyl sulfate with shaking. This resulted in heat development in the mixture and in separation of a precipitate. The reaction was conducted in a nitrogen atmosphere. The reaction was brought to completion and the excess dimethyl sulfate was decomposed by adding a further 15 ml 2 N sodium hydroxide to the reaction mass and heating $\frac{1}{2}$ hour on a water bath. Crystals of (VII) came down after cooling. The yield was quantitative. M.p. 160.5-161° (from ethyl alcohol). According to the literature the m.p. is 161° [1].

2-Methyl-5-methoxy-3-indolylcarboxylic acid (VIII). a) A suspension of 10 g (VII) in a mixture of 350 ml 2 N sodium hydroxide and 150 ml dioxane was boiled 2 hours on an air bath. The dioxane was then distilled off and the precipitate of (VI) was filtered; m.p. 89-90° [1] (2.3 g). On acidifying the mother liquor with acetic acid, (VIII) was obtained. The acid was dried and recrystallized from ethyl alcohol. M.p. 207-208° (with decomp.), in agreement with the literature [1]. Yield 6 g (68.3%).

b) 6.7 g (IX) was dissolved in 50 ml 2 N sodium hydroxide solution, and 6.1 ml dimethyl sulfate was then added dropwise with stirring. The reaction was conducted in a nitrogen atmosphere. The reaction mixture was heated 20 minutes, after which 200 ml 2 N sodium hydroxide and 100 ml dioxane were added. The resultant reaction mixture was refluxed on an air bath for 1½ hours and then worked up as in the preceding experiment. 4.2 g 2-methyl-5-methoxy-3-indolylcarboxylic acid was obtained. Yield of unpurified substance 66.5%, reckoned on (IX). M.p. 207-208° (from alcohol).

2-Methyl-5-methoxyindole (VI). 1.5 g 2-methyl-5-methoxy-3-indolylcarboxylic acid was added to 25 ml glycerol, previously heated to 140°, and the mixture heated 5 minutes at 140°. The reaction solution was cooled and water was added to bring out 2-methyl-5-methoxyindole. Yield 1 g (84.7%). The 2-methyl-5-methoxyindole can also be extracted from the glycerol solution with ether. M.p. 89-90° (from alcohol), in agreement with the literature [1].

2-Methyl-3-acetyl-5-methoxyindole (V). 3 g of (VI), 9.5 g acetic anhydride and 1.5 g freshly calcined sodium acetate were refluxed on an air bath for 5 hours. A brown precipitate came down on cooling. This was heated with water to remove the acetic anhydride and extracted with 2 liters hot water. A white flocculent precipitate of (V) came out on cooling. Yield 2.45 g (68.9%); m.p. 126.5-127.5° (from dioxane). A mixed melting test with the substance obtained in the same investigation by another route did not give a melting point depression.

SUMMARY

The reaction of acetylacetonimine with p-quinone was studied; the known 2-methyl-3-acetyl-5-hydroxybenzofuran and 2-methyl-3-acetyl-5-hydroxyindole were obtained. The structure of the latter was confirmed by reverse synthesis of its methylation product – 2-methyl-3-acetyl-5-methoxyindole.

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Received June 6, 1955

Moscow State University

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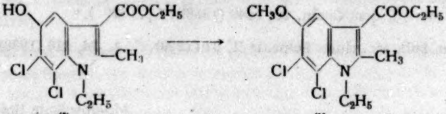
INVESTIGATIONS ON QUINONES

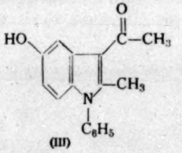
XI. SYNTHESIS OF SUBSTITUTED INDOLES

A. N. Grinev, V. I. Shvedov and A. P. Terentyev

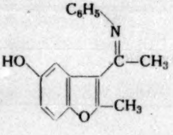
In our preceding papers [1,2] we described the use of the Nenitzescu reaction [3] in the preparation of a number of substituted indoles. A study was made of the reaction of ethyl β-aminocrotonate with 1,4-naphthoquinone and chloroquinone, of ethyl N-methyl-β-aminocrotonate with p-quinone and 1,4-naphthoquinone, and of acetylacetonimine with p-quinone. In the present work we carried out the condensation of 2,3-dichloroquinone with ethyl N-ethyl-β-aminocrotonate and obtained 1-ethyl-2-methyl-3-carbethoxy-5-hydroxy-6,7-dichloroindole (I) in 54.5% yield. This compound darkens when heated in solvents, especially quickly in alkaline solutions, and on methylation with dimethyl sulfate it is transformed in quantitative yield into 1-ethyl-2-methyl-3-carbethoxy-5-methoxy-6,7-dichloroindole (II).



(I) (II)



(III)



(IV)

The reaction of N-phenylacetylacetonimine with p-quinone evidently leads to synthesis of a substituted indole. One of the two structural formulas (III) and (IV) may be proposed for the compound in question on the basis of analytical data. The compound does not change when boiled with hydrochloric acid, and this fact supports the formula of 1-phenyl-2-methyl-3-carbethoxy-5-hydroxyindole (III).

EXPERIMENTAL

1-Ethyl-2-methyl-3-carbethoxy-5-hydroxy-6,7-dichloroindole (I). Solutions of 10 g 2,3-dichloroquinone in 20 ml chloroform and 9.2 g ethyl N-ethyl-β-aminocrotonate in 20 ml chloroform were stirred at room temperature. Considerable heat was evolved and the reaction solution boiled up. The solution was heated one hour on a water bath. The resultant crystals were collected. From the mother liquor, left to evaporate at room temperature overnight, another 3.6 g of (I) was isolated. Yield 9.6 g (54.5%). The compound has good solubility in dioxane, alcohol and acetic acid; it is poorly soluble in chloroform and ether. B.p. 209.5-210° (from dioxane).

Found %: C 53.57, 53.35; H 5.00, 4.93. $C_{14}H_{12}O_3Cl_2N$. Calculated %: C 53.17; H 4.78.

1-Ethyl-2-methyl-3-carbethoxy-5-methoxy-6,7-dichloroindole (II). 4.5 g of (I) was mixed with 35 ml 2 N sodium hydroxide solution in a nitrogen atmosphere. Dioxane was added dropwise to the resultant suspension until theprecipitate dissolved. 2.72 ml freshly distilled dimethyl sulfate was added gradually and with stirring to the solution. Heat was liberated. The reaction mass was stirred 10 minutes and then heated 30 minutes on a water bath. White crystals of (II) were collected. Yield 4.7 g (quantitative). M.p. 127-128° (from dioxane).

Found %: C 54.58, 54.56; H 5.53, 5.54. $C_{15}H_{14}O_3Cl_2N$. Calculated %: C 54.55; H 5.20.

Condensation of p-quinone with N-phenylacetylacetonimine. To a solution of 10.8 g p-quinone in 30 ml dry acetone was added dropwise with stirring 26.3 g N-phenylacetylacetonimine. The reaction solution was heated 1 hour on a water bath and gave 6.2 g yellowish crystals which came out of solution in course of reaction. The mother liquor was evaporated and the residue diluted with ether. The ether dissolved the resinous impurities and the precipitate was filtered off. A further 3.9 crystals was isolated. Judging by the melting point, the substance was identical with that isolated at the start from the reaction solution; a mixed melting test did not show a depression. The crystals are readily soluble in dioxane and alcohol, poorly soluble in ether. The crystals do not undergo any changes when heated with hydrochloric acid. Yield 10.1 g (38.2%). M.p. 232-233° (from ethyl alcohol). Found %: C 76.94, 76.76; H 5.75, 5.75. $C_{17}H_{15}O_2N$. Calculated %: C 76.95; H 5.69.

SUMMARY

The reaction of ethyl N-ethyl-β-aminocrotonate with 2,3-dichloroquinone and of N-phenylacetylacetonimine with p-quinone were studied.

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Received June 6, 1955

Moscow State University

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* T.p. = C. B. Translation pagination.

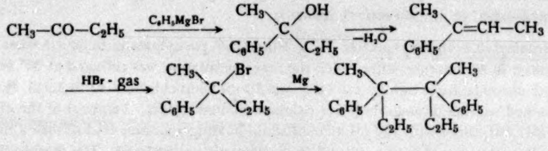
SYNTHESIS AND INVESTIGATION OF NITRO- AND SULFO-DERIVATIVES OF 3,4-DIMETHYL-3,4-DIPHENYLHEXANE

A. M. Khaletsky and A. N. Rudakova

Of the numerous estrogens with a non-steroid structure [1,2] that have been described, the highest activity is possessed by p-hydroxy derivatives of diphenyl- (or o-tolyl)-hexane, hexene, hexadiene ("dienestrol"), heptane ("benzestrol") and heptene [3,5-di-(p-hydroxyphenyl)-5-methyl-2-heptene]. The remaining estrogens, which are derivatives of arylhexene, arylpentene or other classes of organic compounds, posses a lower activity. The above-mentioned highly active estrogens cause tumors in mice after repeated administration and therefore cannot be regarded as completely innocuous [3]. For this reason interest attaches to derivatives of arylbromoethylenes which, although inducing an estrogenic effect in considerably larger doses, do not give rise to secondary action [4]. It is not definitely known, however, which groups or radicals in the molecule are necessary for development of estrogenic activity. Thus, for example, Dodds et al, [5] suggest that any replacement of phenolic hydroxyls in the molecule of an estrogen by other groups (nitro, amino, etc.) leads to a sharp fall in biological activity. At the same time, a recent publication [6] indicates that nitro-substituted diphenylbutanes possess quite high estrogenic activity.

In view of the publication at the end of 1954 of a paper in the foreign literature [7] on the synthesis of meso-p,p-dinitro-3,4-diphenylhexane, we decided to publish our investigations on the synthesis of this compound and of the sodium salt of 3,4-dimethyl-3,4-diphenylhexane-tetrasulfonic acid, especially since the parent hydrocarbon – 3,4-dimethyl-3,4-diphenylhexane – had been obtained by Haung and Lee [7] by radical dimerization by the method of Kharasch and Urry [8], i.e. by pyrolysis of isopropylbenzene in presence of ditert-butyl peroxide, which led to a mixture of products whose separation proved difficult. The authors themselves, however, do not consider the method suitable for practical purposes of synthesis of the estrogen [3,4-dimethyl-3,4-di-(p-hydroxyphenyl)-hexane].

The method of synthesis of the hydrocarbon that we describe below is based on the following reactions:



Nor fortuitous products are formed in this scheme apart from the isomeric compounds which are naturally formed due to the presence of asymmetric carbons.

Starting from phenylmagnesium bromide and methylethyl ketone, we synthesized methylethylphenylcarbinol, which on distillation is partly dehydrated; for complete dehydration it was heated with anhydrous oxalic acid and gave 2-diphenylbutene-2. Hydrobromination of the latter gave, in accordance with the Markovnikov rule, 2-bromo-2-phenylbutane, and this was brought directly (in view of its instability) into reaction with magnesium. Two products with the same composition ($C_{20}H_{26}$) were isolated; one of them was crystalline (yield 11.14%), m.p. 97-98°; the other was liquid (yield 13.2%), b.p. 306-310°.

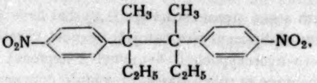
The elementary analysis and the study of derivatives indicate that the hydrocarbons obtained are 3,4-dimethyl-3,4-diphenylhexanes, which are formed by combination of $C_6H_5(C_2H_5)(CH_3)C$- radicals.

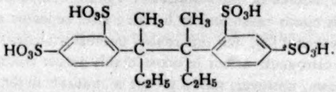
The symmetrical structure of the two halves of the hydrocarbon molecule points to the existence, apart from the d- and l-isomers, of a meso-isomer; the crystalline product is evidently meso-3,4-dimethyl-3,4-diphenylhexane; the liquid is a mixture of the d- and l-isomers.

Nitration of the crystalline product with m.p. 97.98° with nitric acid (d 1.39) in presence of acetic anhydrode gave dinitro-3,4-dimethyl-3,4-diphenylhexane, which after recrystallization from benzene melted at 194-196°.

Sulfonation of the crystalline hydrocarbon with concentrated sulfuric acid gave the sodium salt of 3,4-dimethyl-3,4-diphenylhexane-tetrasulfonic acid.

The structure of the dinitro derivative and of the tetrasulfonic acid are evidently consistent with theoretical ideas about the direction of the action of alkyl derivatives in aromatic compounds:





Tests of the biological activity on mice showed that although dinitro-3,4-dimethyl-3,4-diphenylhexane possesses a high estrogenic activity (20 γ), the tetrasulfo derivative (sodium salt) of the hydrocarbon has low activity. Consideration of the data points to the important role of the nitro group in the molecule of an estrogen.

We wish to convey our thanks to T. A. Melnikova for undertaking the biological tests.

EXPERIMENTAL

2-Phenylbutene-2 was prepared by Tiffeneau's method [9] by dehydration of methylethylphenylcarbinol. The latter was obtained from 18 g magnesium, 100 g bromobenzene and 46 g methylethyl ketone in presence of 0.05 g iodine and 80 ml ether. It was dehydrated with anhydrous oxalic acid (2 g) to give 45.5 g (54% on the methylethyl ketone) 2-phenylbutene-2, b.p. 189-191°.

2-Bromo-2-phenylbutane was obtained by hydrobromination of 2-phenylbutene-2. 45 g of the latter was saturated with 28.5 g dry hydrobromic acid at -2 to +1° to give 73.5 g 2-bromo-2-phenylbutane containing 37.55% bromine (equal to the theoretical amount).

3,4-Dimethyl-3,4-diphenylhexane. 71 g 2-bromo-2-phenylbutane in 50 ml ether was gradually added to 3.8 g magnesium in 40 ml ether, after which the reaction mixture was refluxed at 35° for 3 hours with constant stirring. After decomposition with 50 ml water and 70 ml hydrochloric acid (d 1.12), the ether layer was separated, washed with water and dried over calcined sodium sulfate. Removal of the ether left 26 g yellow oily liquid; this was stirred with 100 ml alcohol while heating and then cooled with a mixture of ice and salt. In this way 3.9 g substance with m.p. 97-98° (from alcohol) was isolated. The mother liquor gave, after distillation of the alcohol and vacuum distillation, 15.4 g substance with b.p. 160-165° at 8 mm. Addition of 30 ml 96% alcohol gave another 1 g substance with m.p. 97-98°; in all, therefore, 4.9 g substance was obtained (11.14% on 2-bromo-2-phenylbutane).

Found %: 91.20, 90.01; H 9.84, 10.20. M 268.5, 260.5. $C_{20}H_{26}$. Calculated %: C 90.15; H 9.71. M 266.0.

From the alcoholic mother liquor after driving off the alcohol was obtained 5.8 g substance with b.p. 306-310° (racemate of 3,4-dimethyl-3,4-diphenylhexane).

Found %: C 89.13, 89.07; H 9.73, 9.87. $C_{20}H_{26}$. Calculated %: C 90.15; H 9.71.

Meso-p,p-dinitro-3,4-dimethyl-3,4-diphenylhexane. 3 g 3,4-dimethyl-3,4-diphenylhexane with m.p. 97-98° in 33 mlacetic anhydride was subjected to nitration with 3.1 ml nitric acid (d 1.39); the temperature rose to 24° during the treatment. The next day the reaction mixture was stirred for one hour with 3 ml water, and the precipitate was recrystallized from benzene; yield 1.8 g (44.8%) substance with m.p. 194-196°.

Found %: N 7.93, 8.12. $C_{20}H_{24}O_4N_2$. Calculated %: N 7.86.

Sodium salt of 3,4-dimethyl-3,4-diphenylhexane-tetrasulfonic acid. 1.2 g meso-3,4-dimethyl-3,4-diphenylhexane with m.p. 97-98° was subjected to sulfonation with 15 ml concentrated sulfuric acid at first at 80-90° and then at 120° for 4 hours. After cooling, the excess of sulfuric acid was neutralized with barium carbonate and the filtrate was decomposed with sodium carbonate. Evaporation of the solution gave a white crystalline powder which was washed with alcohol, dried at 100°; yield 2.3 g (75.64%).

Found %: S 18.73, 18.84. $C_{20}H_{22}O_{12}S_4Na_4$. Calculated %: S 18.98.

SUMMARY

3,4-Dimethyl-3,4-diphenylhexane (meso-compound and racemate) was synthesized from 2-bromo-2-phenylbutane and magnesium; nitration (of meso-isomer) gave a dinitro derivative, and sulfonation gave the tetrasulfo derivative (in the form of the sodium salt).

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Received June 10, 1955

Leningrad Institute of Pharmaceutical Chemistry

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Found %: [illegible]

Sodium salt of [illegible]

Found %: [illegible]

SUMMARY

[illegible]

LITERATURE CITED

[1] [illegible]

[2] [illegible] The Chemistry of [illegible] (Academic Press, [illegible]).

[3] [illegible]

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Received June 10, 1963

THE RATE OF TRANSFORMATION OF 2-KETO-L-GULONIC ACID AND ITS METHYL ESTER INTO L-ASCORBIC ACID IN AN AQUEOUS MEDIUM

V. I. Veksler and G. E. Shaltyko

A study was made earlier [1] of the rate of transformation of the hydrate of diacetone-2-keto-L-gulonic acid (HDAKGA) into L-ascorbic acid (AA) in an aqueous medium in presence of hydrochloric acid. Systems were studied containing 11.15 N hydrochloric acid and HDAKGA in which the total concentration of hydrochloric acid was approx. 3.7 and approx. 5 mole, while the total concentration of HDAKGA was 2 to 2.5 moles per liter of mixture. It was shown that the rate of transformation of HDAKGA into AA under these conditions exceeds the velocity of the corresponding reaction for 2-keto-L-gulonic acid (KGA) in a solution of 5 N hydrochloric acid with a KGA content of 0.05 mole per liter which was studied by Regna and Caldwell [2].

In the present work we studied the rate of transformation of KGA and its methyl ester into AA under the same conditions as in the preceding work [1] on the rate of transformation of HDAKGA. Experiments were also carried out with HDAKGA under the conditions of the study by Regna and Caldwell of the rate of transformation of KGA [2].

EXPERIMENTAL

The general procedure was described previously [1]. The investigation was carried out at 60 and 70° (±0.1°). KGA was synthesized from pure diacetonesorbose (m.p. 76.5-78°) and was also obtained by hydrolysis of technical HDAKGA as described by Reichstein and Grussner [3], m.p. 163-164° (not corrected); the literature gives m.p. 170-171° [2], 171° (corr.) [3]; the methyl ester of KGA was synthesized by the method of V. M. Berezovsky and L. I. Strelchunas [4], m.p. 153°; the HDAKGA had a purity of 98.5%, calculated on the hydrated molecule.

The following reaction mixtures were prepared for the experiments: I. Mixtures of KGA, acetone and 11.15 N hydrochloric acid, corresponding to the composition of previously investigated mixtures [1] containing HDAKGA; acetone was taken in the proportion of 2 moles per mole of KGA (i.e. the amount that is formed on hydrolysis of HDAKGA); the HCl was in the proportion of 2.06 moles per mole KGA. II. Mixtures of KGA and its methyl ester with 11.15 N hydrochloric acid not containing acetone; 2.06 moles HCl per mole of KGA or its ester. III. Mixtures of HDAKGA and KGA with 5 N hydrochloric acid; total concentration of HDAKGA (KGA) in the mixture, 0.05 mole/liter (100 moles HCl per mole HDAKGA or KGA).

Calculation of the velocity constants of the reaction of formation of AA (k_1) in experiments with Mixtures I and II was performed with the simplified formula of Rakovsky for determination of the content of intermediate product in a consecutive reaction of the first order, as proposed by us [1]:

$$k_1 = -\frac{\log\left[e^{-k_2 t} - \frac{b}{a_0}\right]}{0.4343t}, \tag{1}$$

where a_0 is the content of starting substance (KGA or its ester), b is the content of AA at time t. The term k_2 is the velocity constant of decomposition of AA under the investigated conditions, taken from previous work [1]: $k_2^{60} = 1.5\cdot10^{-4}$, $k_2^{70} = 6.4\cdot10^{-4}$. Since these values of k_2 were obtained for the case when the mixture contained acetone (2 moles per mole AA), we made a correction for the rate of decomposition of AA in the absence of acetone. It was found that the values of k_2 did not change substantially when this was done, and were consequently suitable for calculations both of Mixtures I and Mixtures II.

For Mixtures III, where the values of k_1 and k_2 differ to a relatively small extent, the unsimplified Rakovsky formula [5] was used for calculation of k_1:

$$k_1 = -\frac{1}{0.4343t}\log\left[e^{-k_2 t} - \frac{b}{a_0}\cdot\frac{k_1 - k_2}{k_1}\right]. \qquad (2)$$

Values of k_2 for the given conditions were taken from the paper of Regna and Caldwell [2]: $k_2^{59\cdot9} = 4.9\cdot10^{-4}$, $k_2^{69\cdot9} = 14.1\cdot10^{-4}$.

Evaluation of Results

The experimental results of determination of the content of AA in reaction Mixtures I and II are plotted as functions of time and reaction conditions in Figs. 1, 2 and 3. On the basis of these data the velocity constant k_1 of the reaction of formation of AA was calculated from Formula (1). The values of k_1 are characterized by satisfactory constancy in the investigated time intervals: the average deviations from the mean value were 3-10%.

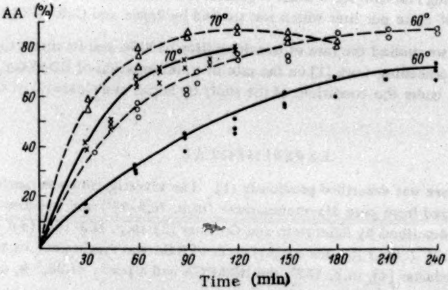

Fig. 1. Formation of L-ascorbic acid from 2-keto-L-gulonic acid in presence of acetone and from the hydrate of diacetone-2-keto-L-gulonic acid by the action of 11.15 N hydrochloric acid.

Continuous curves : KGA (2.06 moles HCl, 2 moles acetone per mole KGA); broken curves: HDAKGA (2.06 moles HCl per mole HDAKGA).

The values found for k_1 are set forth in the table which also shows for comparison the values of k_1 previously obtained for HDAKGA [1]. The table also contains the mean values of k_1 found by Regna and Caldwell [2]. We see from the data that the rates of transformation of KGA and its ester on the one hand and that of HDAKGA on the other hand in presence of concentrated hydrochloric acid are very different. This difference is not observed when using 5 N hydrochloric acid in dilute solutions of KGA and HDAKGA. The difference in reaction rates in presence of 11.15 N hydrochloric acid may be explained by the fact that the investigated reactions do not proceed under identical conditions: KGA and its methyl ester differ from HDAKGA in being insoluble in the cold in concentrated hydrochloric acid. It may be assumed, however, that a role is also played by the difference in chemical structure of the substances: we know that HDAKGA contains a furanose ring [3,7] whereas Reichstein advances (without any evidence) a pyranose ring [3] for KGA. It may be suggested that HDAKGA loses acetone due to hydrolysis and gives initially the furanose form of KGA which exists for a short time and is transformed in presence of HCl into AA at a higher velocity than is the case for KGA in its usual stable form (with a pyranose ring). It may also be suggested that similar considerations apply to the methyl ester of KGA since we know that esters of ketoaldonic acids are very easily hydrolyzed [6] and under the present conditions the rate of transformation of the ester into AA must be governed by the rate of transformation of the KGA formed from it. Additional experimental data would be desirable for a final solution of this problem.

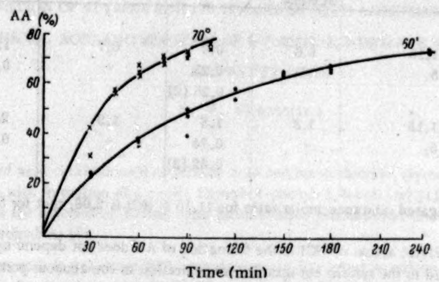

Fig. 2. Formation of L-ascorbic acid from 2-keto-L-gulonic acid in presence of 11.15 N hydrochloric acid in absence of acetone (2.06 moles HCl per mole KGA).

In practice, due to the lower velocity of transformation of KGA into AA, the maximum possible yield of AA must be slightly reduced, while the period necessary for attainment of this yield must increase in comparison with HDAKGA.

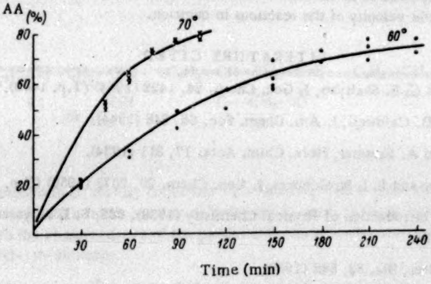

Fig. 3. Formation of L-ascorbic acid from the methyl ester of 2-keto-L-gulonic acid under the action of 11.15 N hydrochloric acid (2.06 moles HCl per mole ester).

Less resin formation is observed in reaction with KGA or its ester than in the experiments with HDAKGA. We established that acetone when heated with HCl under the experimental conditions, does not itself form resins. Consequently the resinification in the case of HDAKGA is not directly associated with the presence of acetone formed by hydrolysis of HDAKGA, but depends upon the characteristic features of the reactions of KGA and HDAKGA.

From the table and from Figs. 1 and 2 we see that in presence of acetone in the reaction mixture in an amount of the order of 2 moles per mole KGA (representing 45% of the total liquid phase), in other words, when the hydrochloric acid is diluted with double the amount of acetone, the reaction velocity is substantially constant.

TABLE

Rate of Formation of L-Ascorbic Acid from 2-Keto-L-gulonic Acid and Its Methyl Ester

Temperature	Concentration of hydrochloric acid (normality)	Magnitude of $k_1 \cdot 10^2$			
		2-Keto-L-gulonic acid (KGA)		Methyl ester of 2-keto-L-gulonic acid	Hydrate of diacetone-2-keto-L-gulonic acid (HDAKGA)
		in presence of 2 moles acetone	in absence of acetone		
60°	11.15	0.6	0.7	0.7	1.2 [1]
	5	–	0.25	–	0.26
			0.25 [2]		
70	11.15	1.8	1.8	1.9	2.7 [1]
	5	–	0.74	–	0.73
			0.82 [2]		

Note. The HCl/ investigated substance molar ratio for 11.15 N HCl is 2.06; that for 5 N HCl is 100.

Hence it follows that the catalytic action of HCl in the formation of AA does not depend upon the total concentration of hydrochloric acid in the system but upon its concentration in the aqueous portion.

SUMMARY

1. Heating of 2-keto-L-gulonic acid and its methyl ester with conc. HCl in the ratio of 2.06 moles HCl to 1 mole substance leads to transformation into L-ascorbic acid at a lower speed than in the case of the hydrate of diacetone-2-keto-L-gulonic acid.

2. The presence of acetone in an amount of the order of 50% of the volume of the liquid phase has no substantial influence upon the velocity of the reactions in question.

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[4] V. M. Berezovsky and L. I. Strelchunas, J. Gen. Chem. 20, 2072 (1950) (T.p. 2145).*

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Received February 9, 1955

Leningrad Institute of Soviet Trade

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* T.p. = C. B. Translation pagination.

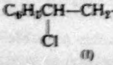
CYCLIC ACETALS

I. CONDENSATION OF STYRENE AND ITS HOMOLOGS WITH ALDEHYDES IN PRESENCE OF HYDROCHLORIC ACID AND REACTION OF 4-PHENYL-1,3-DIOXANE WITH $SOCl_2$, PCl_5 AND FATTY ACIDS

N. V. Shorygina

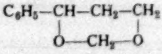
In presence of acid catalysts such as sulfuric acid and boron fluoride, styrene is known to enter into reaction with formaldehyde with formation of a cyclic formal (4-phenyl-1,3-dioxane) [1]. It is believed that in presence of hydrogen halides the reaction of olefins with formaldehyde proceeds less smoothly and tends to yield the corresponding chlorohydrins [2].

In the present work it was shown that both styrene and its closest homologs containing a methyl group in the side chain or in the ring enter with facility into reaction with aldehydes in presence of hydrochloric acid (d 1.19) to give the corresponding meta-dioxanes in yields of up to 90-98% (Table 1). By changing the styrene: :acid : formaldehyde ratio it is possible to direct the reaction, as desired, either towards formation of the dioxane or towards formation predominantly of the partial chlorohydrin. Formation of a partial chlorohydrin both in the form of an intermediate reaction product and in the form of the product of hydrolysis of the acetal in the acid medium indicates the mechanism of formation of cyclic acetals. The intermediate product in formation of the chlorohydrin is the unstable chloromethyl alcohol which enters into reaction with styrene ($CH_2O + HCl \rightarrow [ClCH_2OH]$):



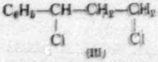
$C_6H_5\underset{\substack{|\\Cl}}{CH}-CH_2-\underset{\substack{|\\OH}}{CH_2}$

(I)



$C_6H_5-\underset{\substack{|\\O-CH_2-O}}{CH-CH_2-CH_2}$

(II)

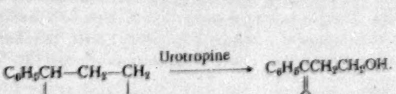


$C_6H_5-\underset{\substack{|\\Cl}}{CH}-CH_2-\underset{\substack{|\\Cl}}{CH_2}$

(III)

The partial chlorohydrin (I) readily condenses with formaldehyde to form the dioxane (II), which in turn breaks down, when heated with a molar amount of hydrochloric acid, to the partial chlorohydrin and formaldehyde. In Table 2 are set forth the characteristics of the partial chlorohydrins obtained from 4-phenyl-, 4-phenyl-2,6-dipropyl- and 4-p-tolyl-1,3-dioxanes.

In order to establish the position of the chlorine, the partial chlorohydrin of 1-phenyl-propanediol-1,3 (3-chloro-3-phenyl-propanol-1) was transformed into 1-phenyl-propanol-3-one-1 by the method of Sommelet [3]:



$$C_6H_5\underset{\substack{|\\Cl}}{CH}-CH_2-\underset{\substack{|\\OH}}{CH_2} \xrightarrow{\text{Urotropine}} C_6H_5\underset{\substack{\|\\O}}{C}CH_2CH_2OH.$$

Formation of a carbonyl compound is confirmed by isolation of a p-nitrophenylhydrazone and a semicarbazone. Examination of the infrared spectrum revealed an absorption band with a maximum at 1630 cm^{-1} which belongs to the carbonyl group of ketones [4]. The negative reaction with dimedon indicates that an aldehyde is

TABLE 1

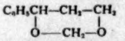
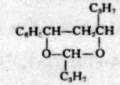
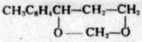
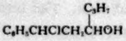
Name of dioxane	Formula	Yield (in %)	Boiling point (mm pressure)	d_4^{20}	n_D^{20}
4-Phenyl-1,3-dioxane	 $C_6H_5CH-CH_2-CH_2$ $O-CH_2-O$	90—98	118—120° (6)	1.1110	1.5331
4-Phenyl-2,6-dipropyl-1,3-dioxane	 C_3H_7 $C_6H_5CH-CH_2CH$ $O-CH-O$ C_3H_7	70—80	175—176 (27)	1.0150	1.4680
4-(p-Tolyl)-1,3-dioxane	 $CH_3C_6H_4CH-CH_2-CH_2$ $O-CH_2-O$	90—95	145—147 (6)	1.080	1.5231

TABLE 2

Name of chlorohydrin	Formula	Boiling point (p in mm)	d_{20}^{20}	n_D^{20}	MR_D		Cl content	
					found	calculated	found	calculated
3-Phenyl-3-chloropropanol-1	$C_6H_5CHClCH_2CH_2OH$	110—112° (8)	1.1479	1.5689	46.49	46.55	19.75	20.58
1-Phenyl-1-chlorohexanol-3	 $C_6H_5CHClCH_2CH(C_3H_7)OH$	128—135 (3)	1.0452	1.5150	61.15	60.40	16.5	16.51
3-p-Tolyl-3-chloropropanol-1	$CH_3C_6H_4CHClCH_2CH_2OH$	118—120 (5)	1.0634	1.5540	55.74	56.00	18.85	19.02
1-Phenyl-1,3-dichloropropane	$C_6H_5CHClCH_2CH_2Cl$	111—113 (3)	1.770	1.5465	50.86	49.89	36.82	37.50

not formed on reaction of the partial chlorohydrin with urotropine. It is highly probable that the reaction would go similarly if sulfuric or another acid were used as catalyst, i.e. with formation as intermediate product of esters of the acids employed.

The above data show that the reation of formation of cyclic acetals from olefins is reversible in its last stage, so that these compounds are unstable and labile in acid media.

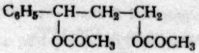
It was established that the rupture of the dioxane ring proceeds with greatest facility in presence of hydrogen halides or of chlorides of organic and inorganic acids. On heating 4-phenyl-1,3-dioxane with an aqueous solution of hydrochloric acid, however, hydrolysis could not be effected and the equilibrium of the reaction was shifted in the direction of formation of the acetal. The reaction equilibrium can be shifted in the direction of complete decomposition only in the event of irreversible binding and removal from the sphere of reaction of one or both products of decomposition. Thus, on heating 4-phenyl-1,3-dioxane with thionyl chloride, the reaction goes with formation of the partial chlorohydrin of 1-phenyl-propanediol-1,3 (I). Introduction into the reaction mixture of 5-10% zinc chloride leads to formation of 1-phenyl-1,3-dichloropropane (III) (yield 50%).

Synthesis of the dihalo- derivative in 85% yield goes easily at 35-40° by reaction of the dioxane with PCl_5 in carbon tetrachloride.

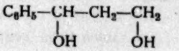
Reaction of cyclic formals with phosphorus pentachloride and thionyl chloride makes possible the transition from olefins to dihalo- derivatives with halogens in the 1,3- position. The carbon chain of the olefins is thereby lengthened by one carbon atom.

Not less interest is attached to the cleavage of cyclic acetals with formation of esters. In previous attempts to acetylate 4-phenyl-1,3-dioxane with acetic anhydride in presence of sulfuric acid at 100°, the ring of the acetal was ruptured at one point [5,6]. Breakdown of the acetal with rupture of the ring at two points calls for change of the other reaction conditions or for another catalyst. Breakdown of cyclic acetals is known to go with facility in presence of HCl or acid chlorides [7]. Sulfuric acid is one of the best catalysts for synthesis of acetals, but it is not active enough to rupture the ring.

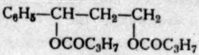
In the present work it was shown that esterification of 4-phenyl-1,3-dioxane can proceed with rupture of the acetal ring at two points [8]. The yield of ester depends upon the reaction conditions and especially upon the catalyst used. Formation of 1-phenyl-propanediol-1,3 diacetate (IV) proceeds at temperatures not exceeding 80-85°, in presence of hydrochloric acid (d 1.19) in the proportion of 10 ml per mole of acetal. Rise of reaction temperature leads to considerable resinification of the reaction mass which unfavorably affects the yield. Hydrolysis of the diacetate leads to the glycol (V).


$C_6H_5-\underset{OCOCH_3}{CH}-CH_2-\underset{OCOCH_3}{CH_2}$

(IV)


$C_6H_5-\underset{OH}{CH}-CH_2-\underset{OH}{CH_2}$

(V)


$C_6H_5-\underset{OCOC_3H_7}{CH}-CH_2-\underset{OCOC_3H_7}{CH_2}$

(VI)

Esterification of 4-phenyl-1,3-dioxane with butyric acid takes place at a higher temperature. The yield of dibutyrate (VI) varies between 50 and 70% (depending upon the catalyst used). The best results are obtained with the ion-exchange resin "Espatit-1" as the catalyst.

EXPERIMENTAL

Synthesis of 1,3-dioxanes. 1 mole styrene (or homolog), 2.5 moles aldehyde and 10 ml hydrochloric acid (d 1.19) were charged into a flask fitted with a stirrer, thermometer and reflux condenser. The reaction mixture was heated on a boiling water bath for 6-7 hours. At the close of the reaction, the mixture had separated into two layers. The lower organic layer was collected, washed with water, with 5% ammonia solution (for removal of the free formaldehyde) and again with water, dried with $CaCl_2$ and distilled in vacuum. Yields and constants of the dioxanes obtained are set forth in Table 1.

Found for 4-p-tolyl-1,3-dioxane %: C 74.13; H 7.79. MR_D 50.40. $C_{11}H_{14}O_2$. Calculated %: C 74.46; H 7.86. MR_D 50.48.

Synthesis of partial chlorohydrins. 1 mole dioxane, 160 ml water and 325 ml hydrochloric acid (d 1.19) were charged into a 750 ml round-bottomed flask. The reaction mixture was heated on a water bath with continuous stirring for 2-3 hours. The organic layer was then collected, diluted with benzene, washed with water, with 5% sodium carbonate solution, and finally several times with water; the benzene and water were then driven off and the residue fractionated in vacuum. Yields of chlorohydrins 50-70%. A considerable amount of resin remained in the flask. The properties of the chlorohydrins are set forth in Table 2.

Condensation of the partial chlorohydrin of 1-phenyl-propanediol-1,3 (3-chloro-3-phenyl-propanol-1) with formaldehyde. 85 g chlorohydrin, 50 ml formalin (36%) and 5 ml hydrochloric acid were charged into a flask. The reaction mixture was heated one hour on a boiling water bath. At the end of the reaction the organic part of the mixture was collected, washed to neutrality with water and sodium carbonate, dried and distilled in vacuum. The main mass of the 4-phenyl-1,3-dioxane came over at 118-120° (6 mm). Yield 98%. Considerable resinification occurred when the amounts of acid and formaldehyde were increased.

Reaction of 4-phenyl-1,3-dioxane with thionyl chloride. 200 g thionyl chloride was charged into a round-bottomed flask fitted with stirrer and reflux condenser, dropping funnel and thermometer. Addition was then made from a dropping funnel, with constant stirring, of 100 g of the dioxane. Due to the exothermic decomposition of the dioxane, the temperature of the reaction mixture rose to 30-35°. After 10-15 minutes, the flask was heated to 50° on a water bath for an hour. Excess thionyl chloride was then distilled off in the vacuum of a water jet pump. The residual oil was diluted with benzene, washed with water and then with 5% sodium carbonate solution; the water and solvent were driven off and the residue fractionated in vacuum. The constants of the prepared chlorohydrin agree with those set forth in Table 2.

Reaction of 4-phenyl-1,3-dioxane with thionyl chloride in presence of $ZnCl_2$. The procedure for the reaction was similar to that in the preceding experiment, with addition of 15 g zinc chloride. 1-Phenyl-1,3-dichloropropane is formed in a yield of up to 50%. Constants are given in Table 2.

Reaction of 4-phenyl-1,3-dioxane with PCl_5. 104 g PCl_5 and 150 ml carbon tetrachloride were charged into a flask, and 40 g 4-phenyl-1,3-dioxane was gradually added through a dropping funnel so that the temperature did not rise above 50°; afterwards water was added from the same dropping funnel to decompose the phosphorus oxychloride. The organic portion of the mixture was then collected, washed with water and sodium carbonate (5%), dried and distilled in vacuum. Yield of 1-phenyl-1,3-dichloropropane 95% (Table 2).

Preparation of the ketol from the partial chlorohydrin (3-chloro-3-phenyl-propanol-1). 17 g of the chlorohydrin, 14 g urotropine and 25 ml ethyl alcohol were charged into a 150 ml round-bottomed flask fitted with a reflux condenser and stirrer. The mixture was stirred one hour without heating and then heated on a water bath at 50-60° for another hour; 40 ml water was added and the resultant complex was decomposed on a boiling water bath. The lower ruby-colored oily layer was collected, diluted with an equal amount of benzene and washed several times with water. The p-nitrophenylhydrazone of 1-phenyl-propanol-3-one-1 was obtained from the benzene solution in the form of golden-orange tablets (from benzene) with m.p. 176-177°.

TABLE 3

Name of dioxane	Yield (%)	Boiling point (pressure in mm)	d	n_D^{20}	MR_D		Saponification number	Volatility	Bromine number
					found	calcd.			
1-Phenyl-propanediol-1,3 diacetate	80—85	154—156° (10)	1.0467 (20°)	1.4929 (20°)	63.37	61.94	—	—	—
1-Phenyl-propanediol-1,3	38—65	156—158 (8)	1.1155 (18°)	1.5417 (18°)	42.86	43.31	—	—	—
1-Phenyl-propanediol-1,3 dibutyrate	50—70	175—180 (3)	1.0351 (17°)	1.5042 (17°)	83.10	82.75	326	0.26	11.7

Found %: N 15.43, 15.43. $C_{15}H_{15}O_3N_3$. Calculated %: N 14.68.

The semicarbazone with m.p. 194-195° was isolated by shaking the benzene solution of 1-phenyl-propanol-3-one-1 with an aqueous solution of semicarbazide.

Found %: N 20.40, 20.36. $C_{10}H_{13}O_2N_3$. Calculated %: N 20.28.

Preparation of the acetate from 4-phenyl-1,3-dioxane. 255 g acetic anhydride, 164 g 4-phenyl-1,3-dioxane and 10 ml hydrochloric acid (d 1.19) were charged into a round-bottomed flask fitted with a reflux condenser. The reaction mixture was heated for 5 hours on a water bath to 80-85°, after which it was run into water; the organic layer was washed with water, with soda and with 5% ammonia solution. The diacetate was dried with $CaCl_2$ and distilled in vacuum. Yield 80-85%. Constants are given in Table 3.

Hydrolysis of 1-phenyl-propanediol-1,3 diacetate. 236 g of the diacetate and 250 ml 16% alcoholic sodium hydroxide solution were charged into a round-bottomed flask fitted with reflux condenser. The reaction mixture was heated on a water bath at 75-80° for 4 hours, cooled and freed from the voluminous precipitate of sodium acetate; the alcohol was removed by distillation. The residue was diluted with dry benzene and freed from sodium acetate, and the benzene was driven off. The glycol was then distilled in vacuum. Yield 58-65%. 1-Phenyl-propanediol-1,3 is a colorless and odorless oil. Constants are in Table 3.

Reaction of 4-phenyl-1,3-dioxane with butyric acid. The reaction was carried out in presence of p-toluene sulfonic acid or of the ion-exchange resin "Espatit-1". Application of an ion-exchange resin as the catalyst reduces resinification of the reaction mass and raises the yield of ester [9]. 164 g 4-phenyl-1,3-dioxane, 176 g butyric acid, 200 ml xylene and 3 g p-toluene sulfonic acid or ion-exchange resin were charged into a round-bottomed flask equipped with stirrer, reflux condenser and Dean and Stark trap. The reaction mixture was heated with continuous stirring on an oil bath at 140-150°. An amount of water close to the theoretical came off in the course of 12 hours. Yield of dibutyrate about 50%. Application of ion-exchange resin cuts down the reaction period to 6 hours, and the yield of ester rises to 70%. The constants are set forth in Table 3.

SUMMARY

1. Styrene and p-methylstyrene were condensed with formaldehyde in presence of hydrochloric acid. The previously undescribed 4-p-tolyl-1,3-dioxane was synthesized.

2. The reversibility of the condensation reaction and the lability of the m-dioxanes were demonstrated. The previously undescribed chlorohydrins of 1-phenyl-, 1-phenyl-3-propyl- and 1-p-tolyl-propanediol-1,3 were synthesized.

3. 4-Phenyl-1,3-dioxane was reacted with thionyl chloride both in presence and absence of $ZnCl_2$. In the first case the partial chlorohydrin was obtained; in the second case the previously undescribed 1-phenyl-1,3-dichloropropane.

4. Reaction of 4-phenyl-1,3-dioxane with PCl_5 gave 1-phenyl-1,3-dichloropropane.

5. The possibility of cleavage of cyclic formals with formation of esters of β-glycols was shown.

1-Phenyl-propanediol-1,3 dibutyrate, not previously described in the literature, was synthesized and characterized.

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THE STRUCTURE AND PROPERTIES OF CELLULOSE

LVI. INVESTIGATION OF THE RELATIVE REACTIVITY OF THE HYDROXYL GROUPS OF CELLULOSE. THE DISTRIBUTION OF METHOXYL GROUPS IN PARTIALLY METHYLATED CELLULOSE PREPARED IN AN ALKALINE MEDIUM

V. Derevitskaya, Yu. Kozlova and Z. Rogovin

One of the fundamental problems of present-day cellulose chemistry is the relative reactivity of the hydroxyl groups. In recent years a series of papers has appeared on the relative reactivity of the hydroxyl groups during acetylation of cellulose [1], xanthation [2], and formation of cellulose ethers [3,4]. Of the three hydroxyl groups of the unit chain of cellulose, the secondary hydroxyls possibly possess more acidic properties (in particular at the second carbon atom) than the primary hydroxyl group. The difference in properties of the hydroxyl groups of cellulose governs the degree of affinity of these groups towards acids and bases.

The character of the reagent and the media in which the reaction takes place must be taken into account when considering the problem of the relative reactivity of the hydroxyl groups of cellulose.

The present work is devoted to a study of the relative reactivity of the hydroxyl groups of cellulose during formation of the methyl ether of cellulose in an alkaline medium. The distribution of the methoxyls between the primary and secondary carbon atoms of partially methylated cellulose, obtained by the action of methyl iodide and dimethyl sulfate on alkali cellulose, was investigated. Various workers have occupied themselves with this problem, but their results have been very conflicting [3-5].

In the present investigation, alkali cellulose was prepared by treatment of cellulose with 18% alkali solution, followed by pressing to three times the weight. (In some experiments the alkali cellulose was washed free from adsorbed alkali with anhydrous butanol [6].) The so-called pure alkali cellulose obtained in this fashion contained an amount of combined sodium corresponding to the value $\gamma = 100$ (γ = number of substituted groups per 100 elementary units). The characteristics of the methyl cellulose obtained from alkali cellulose by the action of methyl iodide at 100° for $3\frac{1}{2}$ hours are set forth in Table 1.

Table 1 shows that the sodium in pure alkali cellulose is nearly completely replaced by the methyl group in a single treatment with methyl iodide. The degree of methylation increases to a relatively insignificant extent when the methyl cellulose is again treated with alkali and again methylated under the same conditions, and the final γ, as calculated from the methoxyl content, never exceeds the γ of the original alkali cellulose calculated on the basis of the sodium content. Methyl celluloses prepared from pure alkali cellulose and from alkali cellulose not washed free from adsorbed alkali have on the average the same degree of substitution.

The distribution of methoxyl groups between primary and secondary carbon atoms was investigated in specimens of methyl cellulose with $\gamma \approx 100$. For this purpose determinations were made of the number of free primary hydroxyl groups by the tritylation method. In some specimens of methyl cellulose the number of free primary hydroxyl groups was also determined by the method of iodination of the nitrates of methyl cellulose. Results are presented in Table 2.

As Table 2 shows, the results of determination of the free primary hydroxyl groups by two parallel methods – tritylation of the methyl cellulose and iodination of the nitrates of methyl cellulose – are in good agreement and show that, in the formation of alkali cellulose and the subsequent methylation, the secondary hydroxyl groups possess the higher reactivity. The number of methoxyl groups attached on the average to one secondary carbon atom

TABLE 1

Speci-men No.	Starting material	Composition of the alkali cellulose γ (from Na content)	First methylation		Second methylation	
			content of OCH_3 (in %)	γ of the methyl cellulose	content of OCH_3 (in %)	γ of the methyl cellulose
1	Cotton linters	113	16.9	96	–	–
2	Ditto	119	16.6	94.3	–	–
3	Cotton	119.2	15.1	85.7	–	–
4	Ditto	120	15.3	87	18.8	106
5	"	120	13.7	77.8	18.5	104
6	"	–	14.9	84.7	17.8	101
7	"	–	15.46	87.7	18.9	107
		(pressed)				
8	"	3.1	15.8	88	–	–
9	"	3	13.9	78	–	–

TABLE 2

Speci-men No.	Starting material	Methylating agent	γ of the methyl cellulose	γ of the tritylated ether of methyl cellulose	Number of $-OCH_3$ groups at the C_6	Total γ of the methyl cellulose nitrate $\gamma_{OCH_3} + \gamma_{ONO_2}$	γ of the iodonitrate of methyl cellulose γ_I	No. of OCH_3 groups at the C_6	Z*
1	Pure alkali cellulose from cotton linters	CH_3I	92.5	78.7	21.3	277.5	77	23	1.59
2	Alkali cellulose from cotton pressed to 3 times the weight		88	76	24	–	–	–	1.33
3	Ditto		86	77.8	22.2	298	80	20	1.54
4	Pure alkali cellulose from cotton		113	70	30	–	–	–	1.38
5	Ditto	$(CH_3)_2SO_4$	107	71	29	–	–	–	1.34
6	Alkali cellulose from cotton pressed to 3 times the weight		78.5	80	20	–	–	–	1.47
7	Ditto		102	77	23	–	–	–	1.71

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*Z is the ratio of the number of methoxyl groups attached on the average to 1 secondary carbon atom to the number of methoxyl groups at a primary carbon atom.

is 1 $^{1}/_{2}$ times as large as the number of methoxyl groups at a primary carbon atom. The character of the distribution of methoxyl groups in the unit chain of methyl cellulose does not depend upon the methylating agent. Thus, for methyl cellulose with γ = 113, obtained by methylation of pure alkali cellulose with methyl iodide, and for methyl cellulose with γ = 107, obtained by methylation with dimethyl sulfate (Samples 4 and 5, Table 2), Z = 1.38 and 1.34, respectively. This shows that methylation in both cases proceeds by substitution of the sodium linked to the cellulose. Nor does the distribution of methoxyl groups change when methylation takes place in presence of adsorbed alkali; consequently, the treatment of alkali cellulose with anhydrous butanol in the preparation of pure alkali cellulose does not lead to redistribution of the sodium atoms in the unit chain of cellulose.

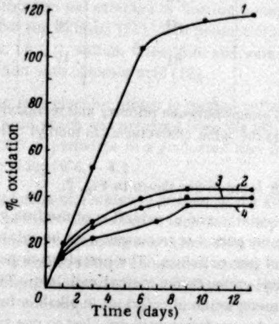

Fig. 1. Oxidation of cellulose (1) and of methyl cellulose with γ 78.5 (2), γ 107 (3) and γ 102 (4) (Specimens 6, 5 and 7 of Table 2) with 0.05 M solution of periodic acid (pH 4–4.1, temperature 20°).

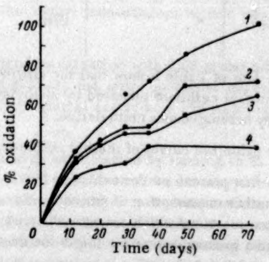

Fig. 2. Oxidation of cellulose (1) and of methyl cellulose with γ 70 (2), γ 74 (3) and γ 90 (4) with 0.05 M periodic acid solution (pH 4.0–4.1, temperature 20°).

There are no reliable methods up to now for the determination of the distribution of alkoxyl groups between the second and third atoms of carbon. We limited ourselves, therefore, to the determination of the number of free glycolic groups in the investigated samples of methyl cellulose by the method of oxidation with periodic acid. The oxidation curves of the original cellulose and of the methyl cellulose are shown in Fig. 1. The methyl cellulose curves indicate that the methoxyl groups attached to the secondary carbon atoms are predominantly located at one of the secondary carbon atoms.

Thus, in methyl cellulose with γ = 78.5, 20 methoxyl groups are located at the C_6 and 58.5 at the secondary carbon atoms (Specimen 6, Table 2). If all the 58.5 methoxyl groups had been located at one of the secondary carbon atoms, the number of free glycolic groups per 100 glucose units would be 41.5, as compared with 42.3 on the basis of oxidation data. In the methyl cellulose with γ = 102 (Specimen 7, Table 2, Curve 4) the number of free glycolic groups per 100 glucose units is 36, whereas it should have been 21 in the event of selective methylation of one of the secondary carbon atoms, while in the event of identical reactivities of the hydroxyl groups of the secondary carbon atoms it should have been 60. We thus have evidence of considerably greater reactivity on the part of one of the secondary hydroxyl groups, and consequently the value of Z in Table 2, calculated on the basis of uniform distribution of methoxyl groups between the secondary carbon atoms, should be considerably higher.

Cellulose was methylated in alkali solution (1% solution of cellulose in 10% caustic alkali) in order to exclude the influence of the cellulose structure on the uniformity of methylation and on the distribution of methoxyl groups. The characteristics of the prepared methyl cellulose and the results of its investigation are set forth in Table 3.

TABLE 3

(Concentration of Cellulose in Solution Equal to 1%)

Specimen No.	Starting material	Methylating agent	γ of the methyl cellulose	γ of the tritylated ether of methyl cellulose	No. of OCH_3 groups at C_6	Z
1	Sulfite cellulose	$(CH_3)_2SO_4$	82	81	19	1.66
2	Viscose rayon	Ditto	82	78	22	1.36
3	Ditto	CH_3I	80	84	16	2.0
4	"	Ditto	74	81	19	1.5

The data of Table 3 show that the distribution of methoxyl groups between primary and secondary carbon atoms in methyl cellulose prepared by methylation in solution has the same character as in methyl cellulose prepared by heterogeneous methylation.

The oxidation curves of methyl cellulose prepared in alkali solution are shown in Fig. 2.

The first plateau on the oxidation curves is considered to mark the end of oxidation of the free glycol groups. Further consumption of periodic acid with further rise in the period of treatment must be related to the peroxidation reactions which are also observed during oxidation of free cellulose. The peroxidation process thus proceeds to a greater degree the larger the number of free hydroxyl groups in the methyl cellulose. The oxidation curves of Fig. 2 show that in methyl cellulose, obtained by methylation of cellulose in alkali solution, the methoxyl groups attached to the secondary carbon atoms are likewise predominantly attached to one of the secondary carbon atoms.

Thus, in methyl cellulose with γ = 74 (Specimen 4, Table 3) 19 methoxyl groups are located at the C_6 and 55 at secondary carbon atoms. The number of free gylcol groups would have been 45 in the event of location of all 55 methoxyl groups at one of the secondary carbon atoms; according to the oxidation data (Curve 3) the number is 47.

EXPERIMENTAL*

The starting substances were cotton linters, cotton treated with 1% alkali solution for 4 hours at 100°, viscose rayon, and sulfite cellulose previously improved in solubility by treatment with hydrochloric acid (10 g/liter) containing 0.1% (on the cellulose weight) of potassium permanganate for one hour at 70°.

Alkali cellulose was prepared by acting on cellulose with 18% alkali solution at 20° for one hour, using a 1:20 bath dilution, followed by pressing to three times the weight. Pure alkali cellulose was obtained by washing the pressed alkali cellulose free from adsorbed alkali with anhydrous butanol. The amount of combined alkali in the pure alkali cellulose was determined by titration [6].

Alkali cellulose was methylated with methyl iodide in a sealed glass ampoule at 100° for 3 1/2 hours [4]. The product was washed with methanol, left overnight in methanol, and washed with acetone. Alkali cellulose was methylated with dimethyl sulfate at room temperature in a medium of toluene for 48 hours (2.66 parts dimethyl sulfate and 17.4 parts toluene per part cellulose). The product was washed with methanol until neutral. Methylation in solution was carried out on viscose rayon or sulfite cellulose which had been dissolved in 10% alkali solution at -8° to -10°. In the prepared 1% solution, the cellulose was methylated with methyl iodide or dimethyl sulfate while stirring at 35-40° for 4 hours. The amount of dimethyl sulfate was varied between 15 and 20 moles, that of methyl iodide between 25 and 30 moles per mole cellulose. The prepared methyl cellulose was precipitated into acidified methanol and washed with methanol and then with acetone. All specimens of methyl cellulose were dried in a drying cupboard at 80° and investigated.

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*With participation of R. G. Krylova.

The content of methoxyl groups was determined by the micro method [7]. Methyl cellulose was tritylated in a medium of pyridine [8 in sealed ampoules at 110-120°. Yield 60-80%.

The content of triphenylmethyl groups in the trityl ether of methyl cellulose was determined by the method of acid saponification [9].

Free primary hydroxyl groups were determined by the method of iodination of the nitrates of methyl cellulose; the latter was exhaustively nitrated with a mixture of nitric (47%, d 1.52) and phosphoric acids (37.7% . d 1.77) and phosphorus pentoxide [10] (15.3%).

The nitrogen content of the nitrates of methyl cellulose was determined in a nitrometer.

Iodination was effected by heating methyl cellulose nitrate with a solution of sodium iodide in cyclohexanone at 120° for 12 hours [11]. The product of iodination was precipitated into ligroine, filtered, and washed with methanol, 0.1 N sodium thiosulfate and water. The iodine in the methyl iodocellulose nitrate was determined by oxidation with chromic acid [12].

The free glycolic groups in methyl cellulose were determined by oxidation with 0.05 molar solution of periodic acid which was prepared from the periodate with acetic acid [3]; the latter operation was effected by putting 13.6 g periodate in a graduated liter flask and adding 20 ml glacial acetic acid and water up to the mark; pH of the solution 4.0- 4.1.

Oxidation of a weighed amount of the air-dry specimen (0.05 g) was effected by running in 25 ml of the prepared periodic acid solution (approximately 400% of the theoretical amount required for complete oxidation of the cellulose) and keeping the closed flask in the dark for the necessary period at room temperature. The methyl cellulose dissolves almost completely during the process of oxidation. The degree of oxidation was estimated from the consumption of periodic acid (titration with 0.1 N sodium arsenite solution). For purposes of calculation, the theoretical consumption of periodic acid for complete oxidation of unsubstituted cellulose was taken as 100%.

SUMMARY

1. A study was made of the distribution of methoxyl groups in partially methylated cellulose prepared by the action of methyl iodide and dimethyl sulfate on alkali cellulose.

2. The secondary hydroxyl groups possess greater reactivity in the reaction of formation of alkali cellulose and subsequent methylation. The number of methoxyl groups corresponding on the average to one secondary carbon atom is approximately $1\frac{1}{2}$ times larger than the number at a primary carbon atom.

Results of determination of the free glycolic groups by the method of oxidation with periodic acid show that the methoxyls are not distributed uniformly between the secondary carbon atoms, but are mostly located at one of those atoms.

3. The distribution of methoxyl groups in methyl cellulose prepared from alkali cellulose does not depend upon the content of adsorbed alkali in the alkali cellulose or upon the methylating agent employed.

4. Methyl celluloses with γ close to 100 are obtained with approximately uniform distribution of methoxyl groups by methylating alkali cellulose in heterogeneous and homogeneous media.

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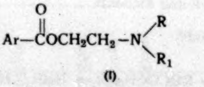
Received May 6, 1955

Moscow Technical Institute

SYNTHESIS OF SOME PHYSIOLOGICALLY ACTIVE ESTERS OF DIALKYLAMINOACETIC ACIDS

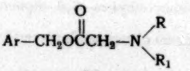
A. L. Remizov and N. V. Khromov-Borisov

Esters of aromatic acids with aliphatic aminoalcohols containing a tertiary amino group are well known as important medicinal substances possessing a characteristic physiological action. They include, in particular, novocaine and an extensive group of analogous esters with the general formula (I), such as the benzoic ester of diethylaminoethanol (III), which possesses a local anesthetic action, the diphenylacetic ester of diethylaminoethanol (IV), and a number of others.



$$\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}OCH_2CH_2{-}N\begin{smallmatrix}R\\R_1\end{smallmatrix}}$$

(I)



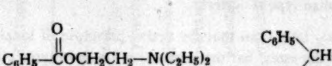
$$\mathrm{Ar{-}CH_2O\overset{\overset{O}{\|}}{C}CH_2{-}N\begin{smallmatrix}R\\R_1\end{smallmatrix}}$$

(II)

It seemed of interest to establish what change occurs in the pharmacological properties of such esters if the aromatic acid* and the aliphatic aminoalcohols from which they are formed are interchanged in respect to acidic and alcoholic functions, i.e. if the acid is replaced by the alcohol corresponding to it, and if the aminoalcohol is replaced by the aminoacid corresponding to it. With this objective, we synthesized a series of esters of dialkylaminoacetic acids of the type of (II) which are isomeric with the above-noted esters (I). Comparison of the structure of esters (I) and (II) shows that their carbon skeletons are identical.

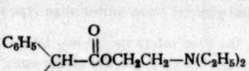
The recent literature contains only a few short communications concerning the pharmacological properties of some esters of tertiary aliphatic aminoacids [1-3].

We obtained the following esters of dialkylaminoacetic acids: the benzyl (V), β,β-diphenylethyl (VI) and the β-phenylethyl (VII) esters of diethylaminoacetic acid; the benzyl (VIII) and β,β-diphenylethyl (IX) esters of N-piperidineacetic acid; the benzyl (X) and β,β-diphenylethyl (XI) esters of N-morpholineacetic acid.



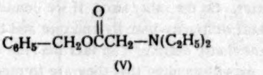
$$\mathrm{C_6H_5{-}\overset{\overset{O}{\|}}{C}OCH_2CH_2{-}N(C_2H_5)_2}$$

(III)



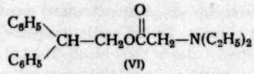
$$\mathrm{\begin{smallmatrix}C_6H_5\\C_6H_5\end{smallmatrix}CH{-}\overset{\overset{O}{\|}}{C}OCH_2CH_2{-}N(C_2H_5)_2}$$

(IV)



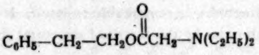
$$\mathrm{C_6H_5{-}CH_2O\overset{\overset{O}{\|}}{C}CH_2{-}N(C_2H_5)_2}$$

(V)



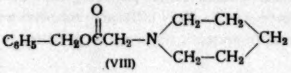
$$\mathrm{\begin{smallmatrix}C_6H_5\\C_6H_5\end{smallmatrix}CH{-}CH_2O\overset{\overset{O}{\|}}{C}CH_2{-}N(C_2H_5)_2}$$

(VI)



$$\mathrm{C_6H_5{-}CH_2{-}CH_2O\overset{\overset{O}{\|}}{C}CH_2{-}N(C_2H_5)_2}$$

(VII)



(VIII)

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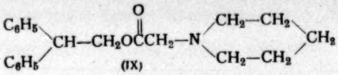
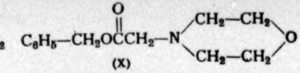
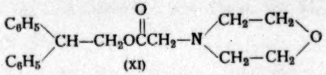
*Here we have in mind acids of the aromatic series, which contain carboxyl groups not only in the ring, but also in the side chain.



(IX)



(X)



(XI)

Compounds (VI), (IX), (X), and (XI) have not been described in the literature and are here synthesized for the first time. We obtained them not only in the form of bases but also in the form of hydrochlorides, picrates, picrolonates and alkyl halides (quaternary ammonium salts). Concerning esters (V), (VII) and (VIII), although they are already known in the form of free bases [as well as the hydrochlorides in the case of (V) and (VIII)], their synthesis has only been described superficially in the form of a general scheme, and no derivatives that could serve for their convenient identification have been obtained [4-6].

We carried out the synthesis of the esters named above by the following general scheme:

1) Preparation of esters of monochloroacetic acid:

$$ROH + ClCH_2COCl \longrightarrow ROCOCH_2Cl + HCl,$$

where ROH is benzyl, β-phenylethyl or β,β-diphenylethyl alcohols.

2) Amination of the esters of monochloroacetic acid:

$$ROCOCH_2Cl + 2NHR_2' \longrightarrow ROCOCH_2NR_2' + NHR_2' \cdot HCl,$$

where NHR'_2 is diethylamine, piperidine or morpholine.

The free bases of the esters formed in the second stage were converted in the usual manner into hydrochlorides, picrates (or picrolonates) and alkyl halides (quaternary ammonium salts).

The β,β-diphenylethyl alcohol (benzhydryl carbinol) used in the work was obtained by reduction of the ethyl ester of diphenylacetic acid by the Bouveault-Blanc method. The monochloroacetic ester, not previously described, was synthesized from it.

Data for the synthesized esters and their derivatives are set forth in the table.

A comparative study of the pharmacological properties of the synthesized esters of type (II) and of the isomeric esters of type (I) showed that all the esters of dialkylaminoacetic acids that were prepared are local anesthetics whose intensity and duration of action are not only inferior but in some cases even slightly superior to those of the corresponding esters of type (I)*. It was also found that type (II) esters possess a considerably lower gangliolytic and general toxic action than type (I) esters.

Consequently, the data refute the widely held view that the active principle of local anesthetics of the novocaine type is not the whole molecule of the ester, but the products of its hydrolytic cleavage in the organism [7]. It is perfectly obvious that products of hydrolysis of esters of types (I) and (II) are entirely dissimilar, both in chemical structure and physicochemical properties. On the other hand, if we consider the whole molecules of both types of esters, we can easily recognize their similarity both in structure and in physicochemical properties, as manifested also in their identical local anesthetic action. The fact that the esters of similar structure (I and II) possess similar physiological action, notwithstanding that they are formed from alcoholic and acid components of widely differing properties and structures, is remarkable in itself. It is a good illustration of the great importance that may be possessed in such cases by the factor of structural similarity.

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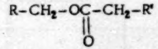
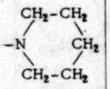
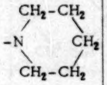
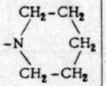
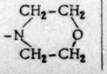
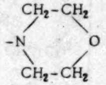
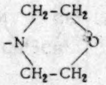
*Pharmacological tests of the synthesized preparations were undertaken by Z. I. Vedeneeva under the direction of S. V. Anichkov.



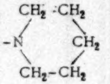
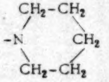
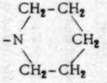
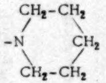
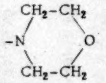
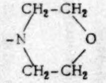
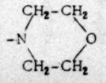
$R-CH_2-OC(=O)-CH_2-R'$

R	R′	Derivative	Melting point	Boiling point	Solubility			
					in water	in ethanol	in acetone	in ether
C_6H_5	-Cl	–	–	130°(11 mm)	insoluble	∞	∞	∞
C_6H_5	$-N(C_2H_5)_2$	base	–	117 (3 mm)	poor	∞	∞	∞
C_6H_5	$-N(C_2H_5)_2$	hydrochloride	88-90°	–	very good	very good	moderate	insoluble
C_6H_5	$-N(C_2H_5)_2$	picrate	77-78.5	–	very poor	decomposes	very good	very poor
C_6H_5	$-N(C_2H_5)_2$	methiodide	109-110	–	very good	very good	crystallizes	insoluble
C_6H_5	$-N(C_2H_5)_2$	ethiodide	88-89	–	ditto	very good	good	insoluble
C_6H_5	$-N(C_2H_5)_2$	ethochloride	112-113.5 (in sealed capillary)	–		good	moderate	insoluble
C_6H_5		base	–	143 (3 mm)	poor	∞	∞	∞
C_6H_5		hydrochloride	135-136	–	very good	very good	good	insoluble
C_6H_5		picrate	137-139	–	insoluble	crystallizes	crystallizes	sparingly soluble
C_6H_5		base	–	152 (2 mm)	poor	∞	∞	∞

Continuation

R	R'	Derivative	Melting point	Boiling point	Solubility			
					in water	in ethanol	in acetone	in ether
C_6H_5		hydrochloride	150-151°	-	very good	very good	moderate	insoluble
C_6H_5		picrate	144-146	-	insoluble	crystallizes	crystallizes	very poor
$C_6H_5CH_2-$	$-Cl$	-	-	135° (7 mm)	ditto	∞	∞	∞
$C_6H_5CH_2-$	$-N(C_2H_5)_2$	base	-	128 (2 mm)	poor	∞	∞	∞
$C_6H_5CH_2-$	$-N(C_2H_5)_2$	hydrochloride	63-65 (softened at 60°)	-	very good (hygroscopic)	very good	very good	insoluble
$C_6H_5CH_2-$	$-N(C_2H_5)_2$	picrate	107-108	-	insoluble	moderate	good	very poor
$C_6H_5CH_2-$	$-N(C_2H_5)_2$	methiodide	70.5-72	-	very good	good	crystallizes	insoluble
$(C_6H_5)_2CH-$	$-Cl$	-	44.5-45.5	-	insoluble	crystallizes	very good	very good
$(C_5H_5)_2CH-$	$-N(C_2H_5)_2$	base	-	-	very poor	∞	∞	∞
$(C_6H_5)_2CH-$	$-N(C_2H_5)_2$	hydrochloride	140-141	-	very good	very good	crystallizes	insoluble
$(C_6H_5)_2CH-$	$-N(C_2H_5)_2$	picrolonate	155-156	-	insoluble	moderate	crystallizes	poor
$(C_6H_5)_2CH-$	$-N(C_2H_5)_2$	methiodide	109-110	-	crystallizes	good	good	insoluble

Continuation

R	R'	Derivative	Melting point	Boiling point	Solubility			
					in water	in ethanol	in acetone	in ether
$(C_6H_5)_2CH-$		base	83-84°	–	very poor	crystallizes	very good	very good
$(C_6H_5)_2CH-$		hydrochloride	132-133	–	very good	very good	good	insoluble
$(C_6H_5)_2CH-$		picrolonate	179-181	–	insoluble	poor	crystallizes	poor
$(C_6H_5)_2CH-$		methiodide	154-155	–	crystallizes	crystallizes	crystallizes	insoluble
$(C_6H_5)_2CH-$		base	63-64	–	very poor	crystallizes	very good	very good
$(C_6H_5)_2CH-$		hydrochloride	162-163	–	good	good	poor	insoluble
$(C_6H_5)_2CH-$		picrate	159-161	–	insoluble	poor	crystallizes	very poor

EXPERIMENTAL

1. Preparation of Esters of Chloroacetic Acid

Benzyl chloroacetate. 11.3 g monochloroacetyl chloride was added to 12.0 g benzyl alcohol with stirring and cooling with tap water. A violent reaction started at once with copious evolution of hydrogen chloride and generation of heat. After the stream of hydrogen chloride had started to weaken appreciably, the reaction mixture was heated on a water bath for 30 minutes. 1 ml methanol was then added and heating continued for another 1-2 minutes (for conversion of unreacted acid chloride into the low-boiling methyl ester). Hydrogen chloride was removed from the liquid (cooled to room temperature) by passing a strong stream of dry air. It was then distilled in vacuum. B.p. 126-127°* (9 mm), 15.5 g (83-85%).

The ester boils at 110° (3.5 mm), 122-123° (7 mm), 126-127° (9 mm), 132° (12 mm). The literature erroneously gives b.p. 147.5° (9 mm) [8].

β-Phenylethyl chloroacetate. The ester was obtained by reacting β-phenylethyl alcohol with chloroacetyl chloride under the conditions described above. Yield 85-90%. B.p. 135° (7 mm).

β,β-Diphenylethyl chloroacetate. The diphenylethyl alcohol (benzhydryl carbinol) required for the synthesis of this ester was obtained by reduction of the ethyl ester of diphenylacetic acid in anhydrous 1-butanol with metallic sodium (Bouveault-Blanc method).** For this purpose a mixture of 9.6 g ethyl ester of diphenylacetic acid and 80 ml anhydrous butanol was gently heated until the solid completely dissolved, after which 2-3 pieces of metallic sodium with a total weight of 5.2-5.5 g were charged into the warm (not over 50°) solution. The flask was at once connected to a condenser and quickly heated until the very violent reaction commenced. Heating was then interrupted for a short time and renewed when the reaction began to abate. After the whole of the sodium had dissolved (with continuous boiling of the reaction mixture), the liquid was cooled slightly and twice shaken with 20 ml water (for extraction of most of the sodium hydroxide), the aqueous layer being separated each time. The butanol solution was acidified with dilute hydrochloric acid until weakly acid to phenolphthalein and then distilled with steam. After the whole of the butanol had been driven off, the residue in the flask was cooled in an ice bath and the soft crystalline mass of diphenyl ethanol was filtered from the aqueous solution of the sodium salt of diphenylacetic acid, washed with cold water on the filter until the filtrate was clear (the wash liquor contained diphenylmethane formed as by-product), dried (in vacuum over sulfuric acid), and recrystallized from ligroine. Yield 4-4.5 g (50-57%).

Depending on the crystallization conditions, diphenylethanol separates either in the form of long needles with m.p. 53-54° (on rapid crystallization from very concentrated solutions) or in the form of stout short prisms with m.p. 61-62°. The second modification is evidently more stable and is more often formed; the literature therefore gives m.p. 59-62° [9,10], although the probability of dimorphism is also indicated [11].

For conversion to the chloroacetate, 2.97 g diphenylethanol was dissolved in 5 ml anhydrous benzene, and the solution was stirred with 1.7 g chloroacetyl chloride. The flask containing the mixture was joined to a reflux condenser closed with a calcium chloride tube. The reaction went with heating on a boiling water bath for $1^{1}/_{2}$-2 hours (until HCl ceased to come off). A few drops of methanol were then added to the flask (to bind the unreacted acid chloride) and heating was continued for another few minutes; after cooling to room temperature, a strong stream of dry air was passed through the reaction mixture until nearly the whole of the solvent was removed and the contents of the flask had been transformed into a solid crystalline mass.

The crude ester (m.p. 40-44°) was recrystallized from 5 ml ethanol. Yield 3.6-3.8 g (87-92%). M.p. 44.5-45.5°.

The substance is easily soluble (especially when heated) in the common organic solvents but insoluble in water.

Found %: Cl 12.94, 12.89. $C_{16}H_{15}O_2Cl$. Calculated %: Cl 12.91.

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*Here, as in all the later experiments, the temperature is corrected for the exposed column of mercury.

**Diphenylethyl alcohol was first prepared by reduction of the benzyl ester of diphenylacetic acid, but the reaction conditions are not described in the original paper [9].

2. Amination of Esters of Chloroacetic Acid

Transformation of the synthesized esters of chloroacetic acid into the corresponding esters of dialkylaminoacetic acids was performed in all cases by a similar method. As an example the preparation of the benzyl ester of diethylaminoacetic acid will be described in more detail.

Benzyl N,N-diethylaminoacetate. 9.25 g benzyl chloroacetate was mixed with 7.5 g diethylamine; the mixture was diluted with 25 ml anhydrous benzene and heated in a flask with a reflux condenser (with calcium chloride tube) on a glycerol bath with gentle boiling for 3-4 hours, and then left overnight.

After dilution with 20 ml ether, crystals of diethylamine hydrochloride were separated by filtration,* and the filtrate (after the solvent had been driven off) was distilled in vacuum. Yield of fraction with b.p. 115-118° (3 mm) 9.0 g (80-82 %). B.p. 144° (11 mm), 156° (17 mm).

The hydrochloride of the ester, prepared from the base and the calculated amount of 30% hydrochloric acid solution in anhydrous alcohol in a medium of acetone-ether, was recrystallized from anhydrous alcohol-ether mixture. M.p. 89-90° (with decomposition). Slowly deliquesces in the air.

The picrate was formed by mixing an ethereal solution of a weighed sample of base with a solution of the calculated amount of picric acid in boiling benzene. It forms long yellow, flat prisms (from benzene and ether). M.p. 77-78.5°.

Found %: N 12.53, 12.64. $C_{19}H_{22}O_9N_4$. Calculated %: N 12.44.

Methiodide. 7.1 g methyl iodide was run into 7.24 g base dissolved in 20 ml acetone. An exothermic reaction commenced after a few minutes and necessitated slight cooling. After an hour the crystals of methiodide were filtered off and washed with ethyl acetate and ether. Yield 11.6 g (98.5%). M.p. 109-110° (from acetone-ethyl acetate mixture).

Found %: I 34.95, 34.50. $C_{14}H_{22}O_2NI$. Calculated %: I 34.95.

Ethiodide. A mixture of 12.3 g base, 10.0 g ethyl iodide and 10 ml anhydrous alcohol was refluxed on a boiling water bath for three hours and then kept at room temperature for 40 hours. After driving off the alcohol in vacuum, the residue was dissolved in water and the aqueous solution, decolorized with a minimum amount of $NaHSO_3$, was freed from unreacted starting substances by shaking with ether (twice) and with benzene (once) and evaporated in vacuum. The glassy residue crystallized after standing in a vacuum desiccator over sulfuric acid for a month. The solid mass was recrystallized from acetone-ethyl acetate mixture (with cooling to -8°). M.p. 88-89°.

Found %: I 33.66, 33.64. $C_{15}H_{24}O_2NI$. Calculated %: I 33.65.

The ethochloride of the benzyl ester of diethylaminoacetic acid was synthesized by reaction of the benzyl ester of monochloroacetic acid with triethylamine. 5.0 g ester, 3 g amine and 5 ml acetone were mixed in a flask fitted with a ground-glass stopper, and the mixture was left at room temperature for 3 days. A yellow oil was formed at first and then changed into a crystalline mass. The latter was filtered, well washed with ethyl acetate and ether, and purified by 2 crystallizations from a mixture of acetone (with a trace of alcohol) and ethyl acetate. In this manner hygroscopic colorless crystals with m.p. 112-113.5° (in a sealed capillary) were obtained.

Found %: Cl 12.31, 12.23. $C_{15}H_{24}O_2NCl$. Calculated %: Cl 12.41.

Benzyl ester of N-piperidineacetic acid. The ester was obtained from benzyl chloroacetate and piperidine in benzene in a yield of 78-80% in the form of a colorless, slightly viscous liquid which distilled at 141-142° (3mm). The hydrochloride of the ester, prepared by neutralization of a weighed amount of the base with the calculated amount of an alcoholic solution of hydrochloric acid, forms colorless scales with m.p. 136-137° (from acetone mixed with ether).

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*From the weight of the hydrochloride of the amine taken into reaction, we can judge the degree of completeness of amination. In the present case, the reaction went to the extent of 93-96%.

The picrate (from equimolar amounts of base and picric acid in boiling benzene) forms bright yellow, elongated prisms (from acetone), m.p. 137-139°.

Found %: N 12.22, 12.05. $C_{20}H_{22}O_9N_4$. Calculated %: N 12.12.

Benzyl ester of N-morpholineacetic acid. Reaction between benzyl chloroacetate and morpholine was carried out in a medium of boiling benzene. Yield of ester with b.p. 153-156° (3 mm) was 80%.

Found %: C 65.77, 65.67; H 7.14, 7.48; N 6.20, 6.14. $C_{13}H_{17}O_3N$. Calculated %: C 66.36; H 7.29; N 5.98.

The hydrochloride (from a solution of the base in a mixture of acetone and ether and the calculated amount of 30% alcoholic HCl) crystallizes from acetone (containing a little alcohol) and ether mixture as colorless plates, m.p. 150-151°.

Found %: Cl 13.16, 13.13. $C_{13}H_{18}O_3NCl$. Calculated %: Cl 13.05.

The picrate (from equimolar amounts of base and picric acid in benzene) crystallizes from acetone as long, bright-yellow prisms with m.p. 144.5-146°.

Found %: N 12.11, 12.30. $C_{20}H_{22}O_9N_4$. Calculated %: N 12.07.

β-Phenylethyl ester of diethylaminoacetic acid. The reaction between β-phenylethyl chloroacetate and diethylamine was effected in anhydrous toluene at 70-80° (2 hours) and 90-100° (1 hour). The solvent was driven off (towards the end in low vacuum) from the filtrate obtained after dilution of the reaction mass with ether and separation of the precipitate (diethylamine hydrochloride). The residue was vacuum distilled.

Yield of fraction with b.p. 135-138° (4 mm) 75-80%. B.p. 128° (2 mm).

The literature [6] reports b.p. of the ester 222° (132 mm), but we failed to reproduce these conditions of distillation.

The hydrochloride separates on neutralization of a weighed amount of the base with anhydrous alcoholic HCl in a medium of ethyl acetate, it forms a colorless oil which crystallizes with difficulty on prolonged rubbing with anhydrous ether or, better, after introduction of a seed. It crystallizes from ethyl acetate in the form of soft needles which are remarkably hygroscopic and quickly deliquesce in the air. M.p. 63-65° (in a sealed capillary it softens at 60°).

Found %: Cl 12.78, 12.80 (by titration). $C_{14}H_{22}O_2NCl$. Calculated %: Cl 13.05.

The picrate (from equimolar amounts of base and picric acid in boiling benzene) crystallizes from benzene in the form of rectangular prisms with m.p. 107-108°.*

Found %: N 12.37, 12.11. $C_{20}H_{24}O_9N_4$. Calculated %: N 12.07.

The methiodide was obtained from 2.35 g base and 2.35 g methyl iodide in 5 ml acetone. The mixture, after standing for 24 hours at room temperature, was diluted with 10 ml acetone and 15 ml ether. The separated oil crystallized on standing in the cold (-8°) for several hours. Yield 3.13 g (83%). M.p. 70.5-72° (from acetone and ether).

Found %: I 33.32, 33.49. $C_{15}H_{24}O_2NI$. Calculated %: I 33.64.

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*Weil [6], who first described the synthesis of this ester, did not obtain its salts or other crystalline derivatives.

β,β-Diphenylethyl ester of diethylaminoacetic acid. A solution of 2.75 g β,β-diphenyl chloroacetate in 8 ml anhydrous benzene, mixed with 1.5 g diethylamine, was refluxed on a glycerol bath at a gentle boil for 6 hours. The cooled reaction mixture was diluted with 15 ml ether; the precipitated diethylamine hydrochloride was separated by filtration, and the filtrate was evaporated in a vacuum (towards the end at 50°) until the weight was constant. The residue was dissolved in 8 ml acetone and neutralized with 0.009 mole HCl (in the form of a 30% solution in anhydrous ethanol). For complete precipitation of the hydrochloride, the mass was diluted with 15 ml ether. The filtered precipitate, which was quickly washed with ether, was dried in vacuum over solid KOH. M.p. 140-141° (from acetone ether).

Found %: Cl 10.23, 10.32. $C_{20}H_{26}O_2NCl$. Calculated %: Cl 10.19.

The free base of the ester, isolated from the salt with aqueous ammonia and by extraction with ether, remained after removal of the solvent as a viscous, colorless oil which could not be distilled without decomposition in the vacuum of a water jet pump.

Picrolonate * (from a solution of the base in acetone and a saturated solution of the calculated amount of picrolonic acid in boiling ethanol) crystallizes from acetone in the form of rectangular, pale yellow prisms with m.p. 155-156°.

Found %: C 62.67, 62.73; H 5.84, 5.71; N 12.31, 12.36. $C_{30}H_{33}O_7N_5$. Calculated %: C 62.60; H 5.78; N 12.17.

The methiodide was prepared from 3.11 g base and 2.8 g methyl iodide dissolved in 25 ml acetone-ether mixture (1:4). A crystalline precipitate came down after 48 hours (at room temperature). Yield 4.03 g (89%). M.p. 109-110° (from acetone-ethyl acetate mixture).

Found %: I 27.94, 27.62. $C_{21}H_{28}O_2NI$. Calculated %: I 28.00.

β,β-Diphenylethyl ester of N-piperidineacetic acid. The reaction of diphenylchloroacetate with piperidine was carried out in a medium of boiling benzene for 5-6 hours. After removal of the precipitate of piperidine hydrochloride and removal of the solvent in vacuum, the residue crystallized. It was dissolved in the minimum amount of boiling ethanol and, by cooling of the solution, it was isolated in the form of square plates with m.p. 82-83°. Yield 85%.

Found %: C 77.93, 78.10; H 7.70, 7.81; N 4.39, 4.33. $C_{21}H_{25}O_2N$. Calculated %: C 77.99; H 7.79; N 4.33.

The hydrochloride, precipitated from a solution of the base in ethyl acetate with the calculated amount of a 30% alcoholic solution of HCl and recrystallized from acetone ether, melts at 92-95° and contains 1 molecule of water. It loses the greater part of the water when dried in vacuum over H_2SO_4, but is not completely dehydrated until heated to 105-110°.

Found %: H_2O 4.86; Cl 9.30, 9.27 (by titration). $C_{21}H_{28}O_3NCl$. Calculated %: H_2O 4.77; Cl 9.39.

After drying to constant weight the salt melts at 132-133°.

Found %: Cl 9.90, 9.92 (by titration). $C_{21}H_{26}O_2NCl$. Calculated %: Cl 9.86.

The picrolonate * (from a solution of the base in acetone and a hot concentrated solution of the calculated quantity of picrolonic acid in alcohol) forms pale yellow, short prisms with m.p. 176-178° (from glacial acetic acid).

Found %: N 12.00, 12.14. $C_{31}H_{33}O_7N_5$. Calculated %: N 11.92.

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*A crystalline picrate could not be obtained.

Methiodide (from 2.4 g base in 6 ml acetone and 1.42 g methyl iodide in 6 ml ether after standing for 2 days at room temperature); a crystalline powder (yield 96%) with m.p. 154-155° (from ethanol).

Found %: I 27.27, 27.29. $C_{22}H_{28}O_2NI$. Calculated %: I 27.27.

β,β-Diphenylethyl ester of N-morpholineacetic acid. The ester was prepared in a similar fashion to the ester of piperidineacetic acid. The base forms short needles (from aqueous alcohol) with m.p. 63-64°.

Found %: C 73.93, 73.81; H 7.05, 7.16; N 4.21, 4.28. $C_{20}H_{23}O_3N$. Calculated %: C 73.82; H 7.13; N 4.30.

Hydrochloride. Lustrous scales (from methanol-acetone). M.p. 161-163°.

Found %: Cl 9.74, 9.67 (by titration). $C_{20}H_{24}O_3NCl$. Calculated %: Cl 9.80.

Picrate. From equimolar amounts of base and picric acid in boiling benzene. Vivid yellow, hexagonal prisms with m.p.159-160.5° (from acetone-methanol).

Found %: N 10.39, 10.13. $C_{26}H_{26}O_{10}N_4$. Calculated %: N 10.11.

SUMMARY

1. 7 esters of dialkylaminoacetic acids were prepared: the benzyl (I), β-phenylethyl (II), β,β-diphenylethyl (III) esters of N,N-diethylaminoacetic acid; the benzyl (IV) and β,β-diphenylethyl (V) esters of N-piperidineacetic acid; the benzyl (VI) and β,β-diphenylethyl (VII) esters of N-morpholineacetic acid. The following preparations were not previously described in the literature: the free bases of esters III, V, VI and VII; the hydrochlorides of the esters II, III, V, VI and VII; the picrates of esters I, II, IV, VI and VII; the picrolonates of esters III and V; the methiodides of esters I, II, III and V; the ethiodide and ethochloride of ester I; and the β,β-diphenylethyl ester of chloroacetic acid.

2. It was established that all the synthesized aminoesters are local anesthetics whose strength and duration of action are similar to those of their isomeric esters of the corresponding dialkylaminoethanols possessing the same hydrocarbon skeleton (i.e. diethylamino-, N-piperidine- and N-morpholine-β-ethanols).

3. The absence of appreciable difference in the anesthetic action of esters of aminoacids and of aminoalcohols (in the former case with fatty aromatic alcohols and in the second with aromatic or fatty aromatic carboxylic acids) refutes the theory that the local anesthetic activity of esters of the novocaine type depends not on the properties of the whole ester molecule which is exceptionally quickly broken down in the organism, but on the products of its hydrolytic breakdown.

The products of hydrolysis of esters of both types differ so markedly, both in chemical and physical properties, that the probability of a common basis in their physiological action is extremely remote.

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Received June 7, 1955

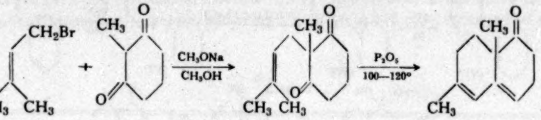
Institute of Experimental Medicine
of the Academy of Medical Sciences
of the USSR

SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO THE STEROIDS

XXXV. CONDENSATION OF CYCLIC ALLYL HALO- DERIVATIVES WITH CYCLIC 2-METHYL-1, 3-DIKETONES AND INTRAMOLECULAR CYCLIZATION OF THE RESULTANT COMPOUNDS TO KETONES CONTAINING THE HYDROGENATED SKELETON OF PHENANTHRENE, CHRYSENE AND CYCLOPENTANOPHENANTHRENE WITH AN ANGULAR METHYL GROUP

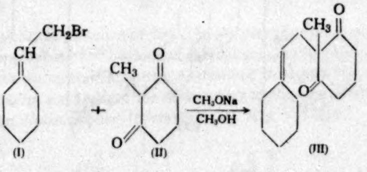
I. N. Nazarov, G. P. Berkholetova, S. N. Ananchenko,
I. V. Torgov and G. V. Aleksandrova

The condensation was previously described [1] of allyl halo-derivatives with methyldihydroresorcinol and cyclization of the resultant substituted allyl derivatives of cyclohexane-1,3-dione to bicyclic ketones with an angular methyl group, taking place on heating with a little phosphorus pentoxide:



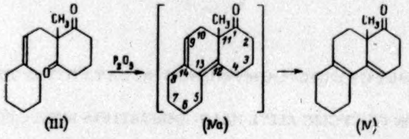
The objective of the present work was the extension of these reactions to other systems in order to prepare polycyclic ketones with an angular methyl group which could be utilized for synthesis of steroid compounds and related substances.

Condensation of β-cyclohexylideneethyl bromide (I) with the Na-derivative of 2-methylcyclohexanedione-1,3 (II) in anhydrous methanol gave a 57% yield of the crystalline 2-methyl-2-(β-cyclohexylideneethyl)-cyclohexanedione-1,3 (III):



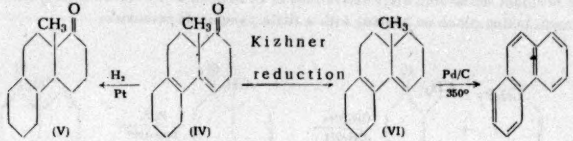
This reaction also goes in aqueous acetone solution with the K-derivative, obtained by the action of potassium carbonate on it. The yield of diketone (III) in this case is 46%, but by working up of the mother liquor with a fresh portion of potassium carbonate and bromide (I), the yield can be raised to 58%.

Heating of diketone (III) in presence of 8-10% (by weight) of phosphorus pentoxide at 110° in vacuum gives a 55% yield of 11-methyl-1-keto-$\Delta^{4,13}$-decahydrophenanthrene (IV) in the form of a yellow liquid, crystallizing when cooled with solid carbon dioxide:

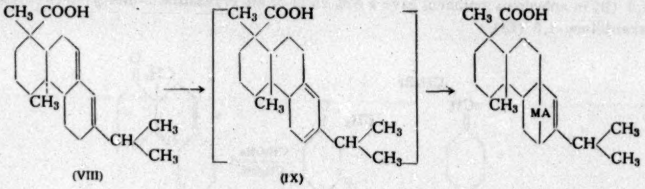


Cyclization of diketone (III) also takes place on heating with phosphorus pentoxide in acetic anhydride solution at 140°, but the reaction does not go with acetic anhydride alone. Attempts to realize the cyclization of diketone (III) by heating with phosphorus pentoxide in pyridine (115-120°, 5 hours) and with diethylamine (120°, 15 hours) were unsuccessful, the original substance being recovered. Heating of diketone (III) with phosphorus oxychloride in pyridine or benzene led to complete resinification of the product.

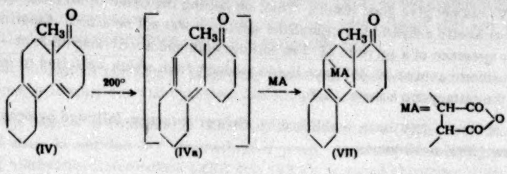
Hydrogenation of ketone (IV) in presence of Pt catalyst results in absorption of 2 moles hydrogen and formation of 11-methyl-1-ketoperhydrophenanthrene (V), possibly in the form of a mixture of stereoisomers. Kizhner reduction of ketone (IV), followed by dehydrogenation of hydrocarbon (VI) with 10% palladium on carbon at 350°, led to formation of phenanthrene. Consequently, the structure of ketone (IV) as a derivative of hydrogenated phenanthrene is not in doubt:



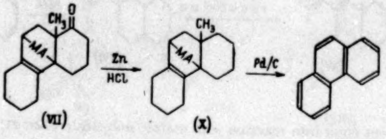
The position of the double bonds in ketone (IV) was established with very much greater difficulty. The original formula (IVa) was rejected since ketone (IV) does not react with maleic anhydride, even when heated to 170°. At 200°, however, this condensation takes place easily and a 60% yield of the crystalline anhydride (VII) is obtained. It is known that abietic acid (VIII) enters into reaction with maleic anhydride only at elevated temperature (about 200°) with preliminary isomerization to levopimaric acid (IX):



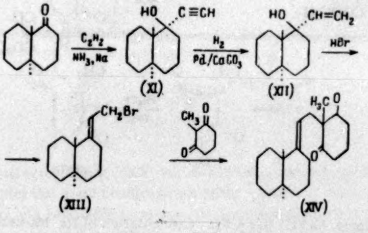
A similar behavior of the tricyclic ketone that we obtained on condensation with maleic anhydride (MA) is evidence of the heteroangular position of the double bonds, i.e. in conformity with formula (IV):



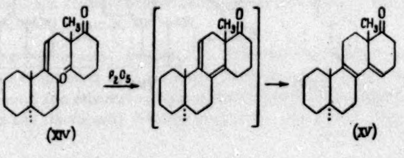
The structure of the anhydride (VII) was confirmed by Clemmensen reduction to the anhydride (X) and dehydrogenation of the latter with 10% palladium on carbon with formation of phenanthrene:



The reactions described above were utilized also for preparation of the tetracyclic ketone (XV) with the hydrogenated skeleton of chrysene. Condensation of trans-*a*-decalol with sodium acetylide in liquid ammonia gave a 96% yield of trans-1-ethynyl-1-decalol (XI), which was transformed, by selective hydrogenation with Pd catalyst, into trans-1-vinyl-1-decalol (XII). Reaction of the carbinol (XII) with gaseous hydrogen bromide led to nearly quantitative yield of *β*-(trans-*a*-decalidene)-ethyl bromide (XIII). Condensation of this bromide with the Na-derivative of 2-methylcyclohexanedione-1,3 (II) in anhydrous methanol led to formation of 2-methyl-2-[*β*-(*a*-decalideneethyl)]-cyclohexanedione-1,3 (XIV) in 78% yield reckoned on the reacted diketone (II):

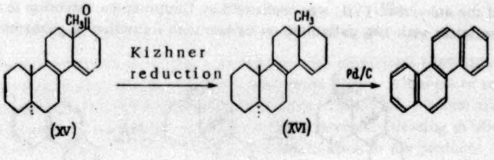


Heating of diketone (XIV) in presence of 25% (by weight) phosphorus pentoxide at 120-130° in vacuum leads to the crystalline 13-methyl-$\Delta^{8,14(15)}$-allocardochrysadienone-17a (XV) [2] in about 10% yield. A liquid mixture of stereoisomers with the same composition is obtained in about 17% yield, in addition to the crystalline isomer. From the liquid mixture was isolated the dinitrophenylhydrazone of the crystalline isomer with m.p. 233-235° and a small amount of dinitrophenylhydrazone with m.p. 204-206°.



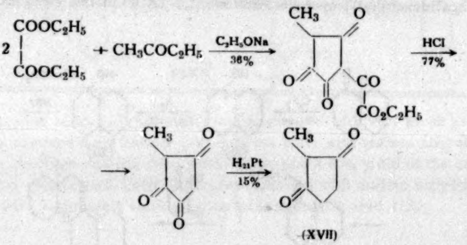
Attempts to increase the yield of the tetracyclic ketone (XV) by changing the conditions of cyclization of the diketone (XIV) did not give good results. Thus, on boiling the oxide of diketone (XIV) with phosphorus pentoxide in xylene or acetic anhydride, a crystalline substance was not obtained. Experiments on cyclization of diketone (XIV) in presence of a mixture of 75% sulfuric acid and acetic anhydride at -6 to -10°, and also with anhydrous hydrofluoric acid at 30-40° gave liquid products from which we failed to isolate even the dinitrophenylhydrazine of the tetracyclic ketone (XV).

The structure of ketone (XV) was established by Kizhner reduction followed by dehydrogenation of the resultant hydrocarbon (XVI) to chrysene:

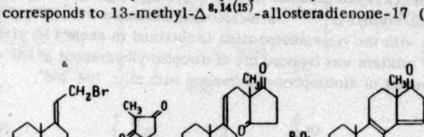


Ketone (XV) does not enter into reaction with maleic anhydride even at 190°, which points to a heteroannulised position of the double bonds. In contrast to the behavior of ketone (IV), hydrogenation of the tetracyclic ketone (XV) does not go smoothly; only one hydrogen molecule is taken up and a non-crystalline mixture of isomers is formed.

Subsequently we carried out the synthesis of the tetracyclic ketone (XIX) of the cyclopentanophenanthrene series, starting from the bicyclic bromide (XIII) and 2-methylcyclopentanedione-1,3 (XVII). The latter was prepared by the method of Orchin and Butz [3] from methylethyl ketone and diethyl oxalate:



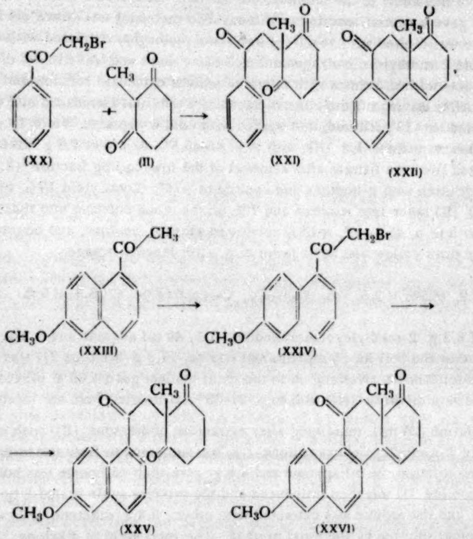
The total yield of diketone (XVII) was 4.3%. Condensation of its Na-derivative with the bromide (XIII) in anhydrous methanol led to 2-methyl-2-[β-(trans-α-decalideneethyl)]-cyclopentanedione-1,3 (XVIII) in 40% yield. Heating of the latter in vacuum in presence of phosphorous pentoxide at 120-130° gave a liquid substance whose analysis closely corresponds to 13-methyl-$\Delta^{8,14(15)}$-allosteradienone-17 (XIX):



The small amounts of substance prevented isolation of ketone (XIX) in the analytically pure form, and it was obtained as the dinitrophenylhydrazone. On the basis of analogy with ketones (IV) and (XV), we assign to it the formula of (XIX) with a heteroannulised position of the double bonds.

Consequently, our method for building up polycyclic systems has been extended to the preparation of ketones of the hydrophenanthrene, hydrochrysene and cyclopentanohydrophenanthrene series.

It was also of great interest to establish the possibility of cyclization of cyclic 1,3-diketones containing in the 2-position an allyl chain in addition to a ketomethylene group. As model substances for this purpose, we selected derivatives of methyldihydroresorcinol (XXI) and (XXV), prepared according to the following scheme:



Condensation of ω-bromoacetophenone (XX) and of 1-bromoacetyl-6-methoxynaphthalene (XXIV) with methyldihydroresorcinol (II) under the usual conditions gives the crystalline triketones (XXI) and (XXV) in a yield of about 50%; we have not yet been able to realize the cyclization of these to the corresponding diketones (XXII) and (XXVI) under our experimental conditions (heating with phosphorus pentoxide in a solvent or without a solvent, with phosphoric acid, etc.).

EXPERIMENTAL

1-Vinylcyclohexanol-1 was obtained by hydrogenation of 1-ethynylcyclohexanol-1 by the method developed in our laboratory [4]. B.p. 66-67° at 12 mm, n_D^{20} 1.4765.

2-Methylcyclohexanedione-1,3 (methyldihydroresorcinol) was obtained in 45% yield by methylation of cyclohexanedione (dihydroresorcinol) [5], m.p. 207-208°.

Preparation of β-cyclohexylideneethyl bromide (I). Hydrogen bromide was passed at 0° into a solution of 40 g vinylcyclohexanol-1 in 40 ml ether until the weight increase was 39 g (50% excess), after which the mixture was stirred at 0° for one hour. The ethereal solution of the bromide was separated, washed 3 times with water, dried with potassium carbonate and fractionally distilled in vacuum. Yield 48 g (80%) β-cyclohexylideneethyl bromide (I) in the form of a colorless, mobile liquid with a sharp lachrymatory odor, rapidly darkening and becoming turbid on standing. B.p. 67-69° at 3 mm, n_D^{20} 1.5620, d_4^{20} 1.2754, MR_D 45.5; calc. 44.3.

Found %: Br 42.5, 42.2. $C_8H_{13}Br$. Calculated %: Br 42.3.

Condensation of 2-methylcyclohexanedione-1,3 (II) with β-cyclohexylideneethyl bromide (I). a) 16.6 g 2-methylcyclohexanedione-1,3 (II) was added with stirring to a solution of sodium methoxide (from 3 g sodium) in 60 ml anhydrous methanol, and the mixture boiled 10-15 minutes. The resultant solution of the Na-derivative of 2-methylcyclohexanedione-1,3 was cooled, and 28 g freshly distilled β-cyclohexylidene-ethyl bromide (I) was added with stirring at 10° for 1 hour. After 20-30 minutes sodium bromide began to separate. After addition of the whole of the bromide, the mixture was stirred 1 hour at 10° and 1½ hours at 15-20° until a sample gave a neutral reaction to litmus. The methanol was driven off in vacuum at 30-35°, and the viscous residue was diluted with 25-30 ml water and thoroughly extracted with ether; during this step, the poorly ether-soluble 2-methylcyclohexanedione-1,3 came down and was filtered off (3.7 g, m.p. 198-200°). The ethereal solution was washed 3 times with saturated sodium carbonate solution and with water and dried with sodium sulfate. After driving off the ether in vacuum, a seed was introduced and the product crystallized. The crystals were cooled to −10°, filtered, and washed with cold n-heptane. Yield 13 g 2-methyl-2-(β-cyclohexylideneethyl)-cyclohexanedione-1,3 (III) with m.p. 45-45.5°. A further 4.5 g diketone (III) with m.p. 38-40° could be isolated from the filtrate after removal of the low-boiling fraction (3.2 g, b.p. 40-45° at 3 mm, n_D^{20} 1.4705), dilution with n-heptane and cooling to −70°. Total yield 57%, reckoned on the 2-methylcyclohexanedione-1,3 (II) taken into reaction and 72% on the dione entering into reaction. The diketone (III) forms white crystals with m.p. 45.5-46°, readily soluble in alcohol, acetone, and benzene, less soluble in ligroine. The substance turns yellow and has a lower m.p. after lengthy storage.

Found %: C 76.9, 76.95; H 9.5, 9.5. $C_{15}H_{22}O_2$. Calculated %: C 76.9; H 9.5.

b) A mixture of 8.3 g 2-methylcyclohexanedione-1,3, 40 ml acetone and 9.2 g potassium carbonate in 24 ml water was stirred at the boil for 25 minutes and cooled; 11.3 g bromide (I) was at once added, and stirring was then resumed for 2 hours. Working up in the usual manner gave 4.35 g diketone (III) with m.p. 36-38.5°; another 1.25 g of less pure diketone (III) with m.p. 31-35° was isolated from the mother liquor.

The aqueous solution (25 ml), remaining after extraction of diketone (III) with ether and containing excess of K-derivative of 2-methylcyclohexanedione-1,3, was subjected to fresh treatment with bromide (I). A mixture of this aqueous solution, 25 ml acetone and 4.6 g potassium carbonate was boiled while stirring for 10 minutes. 7.9 g bromide (I) was then introduced and the mixture again boiled 2 hours; the acetone was driven off in vacuum, and the residue was extracted with ether. 3.3 g diketone (III) with m.p. 33-36° was isolated from the ethereal solution by the usual method. The total yield of diketone (III) was 8.9 g (58%).

Cyclization of 2-methyl-2-(β-cyclohexylideneethyl)-cyclohexanedione-1,3 (III). a) A well-stirred mixture of 5.1 g diketone (III) and 0.5 g phosphorus pentoxide was heated in a Claisen flask in vacuum for 20 minutes at 110° with periodical shaking. During this period the refractive index of the liquid reaction mixtrue changed from 1.514 to 1.555. The product was cooled, neutralized with sodium carbonate colution and extracted with ether. The ethereal extract was washed with sodium carbonate solution and then with water and dried with sodium sulfate. Distillation in vacuum gave 2.7 g (57%) 11-methyl-1-keto-$\Delta^{4,13}$-decahydrophenanthrene (IV) in the form of a viscous, light-yellow liquid, turning yellow and polymerizing on standing. B.p. 136-137° at 1 mm, n_D^{20} 1.5550. Resinous residue 1.9 g.

Found %: C 82.8, 82.95; H 9.25, 9.3. $C_{15}H_{20}O$. Calculated %: C 83.3; H 9.3.
Semicarbazone: white crystals (from alcohol) with m.p. 223-224.5°.
Found %: N 15.4, 15.6. $C_{16}H_{23}ON_3$. Calculated %: N 15.4.

b) A mixture of 3 g diketone (III), 0.5 g phosphorus pentoxide and 5 ml acetic anhydride was heated at 140° for 5 hours in a nitrogen atmosphere with periodic shaking. The acetic anhydride was driven off in vacuum, and the residue was diluted with 10 ml water and extracted with ether. The ethereal extract was washed with sodium carbonate solution and with water, and dried with sodium sulfate. Fractionation of the product in vacuum gave 1.3 g (47%) ketone (IV) with b.p. 154-156° at 2.5 mm, n_D^{20} 1.5530. Resinous residue 1.3 g.

Hydrogenation of ketone (IV). 0.75 g ketone (IV) was hydrogenated in solution in 6 ml alcohol in presence of Adams catalyst. Hydrogenation started immediately and in the course of $1\frac{1}{2}$ hours, 153 ml hydrogen (18° and 760 mm) was absorbed, after which the hydrogen uptake sharply slowed down and hydrogenation ceased. Removal of the alcohol and distillation of the product in vacuum led to 0.45 g 11-methyl-1-keto-perhydrophenanthrene (V) in the form of colorless, viscous liquid with b.p. 130-131° at 2 mm, n_D^{20} 1.5260.

Found %: C 81.5, 81.6; H 10.7, 10.7; $C_{15}H_{24}O$. Calculated %: 81.8; H 11.0.
Semicarbazone: colorless crystals with m.p. 243-243.5°.
Found %: N 15.1, 15.4. $C_{16}H_{27}ON_3$. Calculated %: N 15.15.

Reduction of ketone (IV) by the Kizhner method. A mixture of 1.7 g ketone (IV), 5 ml dioxane, 1.2 ml hydrazine hydrate and 5 ml diethylene glycol was heated a few minutes on a water bath; the mixture was transferred to a Favorsky flask and a solution of sodium diethylene glycolate (from 1.4 g Na in 25 ml diethylene glycol) was added. In the course of 2 hours the reaction mass was gradually heated to 205° and it was then held at this temperature for 7 hours. The entire operation was performed in a stream of nitrogen. Water and a readily volatile fraction came over in a receiver. At the close of the heating, the contents of the flask and the distillate were diluted with 50 ml water and extracted with ether. The combined ethereal extract was washed with 10% hydrochloric acid and water. Distillation gave 1.1 g 11-methyl-$\Delta^{4,13}$-decahydrophenanthrene (VI) with b.p. 116-117° at 2 mm, n_D^{25} 1.5455.

Dehydrogenation of hydrocarbon (VI). A mixture of 1.1 g hydrocarbon (VI), prepared in the preceding experiment, 5 ml dry benzene and 0.5 g 10% palladized carbon was heated in a metal ampoule at 350-355° for 6 hours in a nitrogen atmosphere. After filtration and distillation of the solvent, the residue was a mobile, dark yellow, fluorescent liquid. Cooling to −70° brought down crystals (18 mg) with m.p. 95.5-96°, not giving a depression of melting point when mixed with a specimen of pure phenanthrene (m.p. 99.5°). The picrate has m.p. 142.5° and likewise does not give a depression in admixture with the picrate of pure phenanthrene (m.p. 144°).

Condensation of 11-methyl-1-keto-$\Delta^{4,13}$-decahydrophenanthrene (IV) with maleic anhydride. a) At 170°. A solution of 1 g ketone (IV) and 0.45 g maleic anhydride in 10 ml dry benzene was heated in a metal ampoule at 170° for 7 hours. After driving off the benzene, addition of ligroine and cooling to −70°, 0.2 g crystals with m.p. 127-129° separated (maleic acid). b) At 200°. A solution of 1 g ketone (IV) and 0.45 g maleic anhydride in 6 ml benzene was heated in presence of a trace of pyrogallol in a metal ampoule at 190-200° for 5 hours. After the benzene had been driven off, the residual viscous mass was dissolved in 2 ml acetone and cooled. The separated crystals were filtered and twice washed with ligroine. Yield 0.85 g (60%) anhydride (VII) with m.p. 150-158°. After two crystallizations from a mixture of acetone and heptane (1:3) the pure anhydride (VI) has m.p. 163.5-164°. Easily soluble in benzene and acetone, poorly soluble in ether and ligroine.

Found %: C 72.6, 72.65; H 7.1, 7.0. $C_{19}H_{22}O_4$. Calculated %: C 72.6; H 7.05.

Saponification of the anhydride (VII). A suspension of 0.2 g anhydride (VII) in 2 ml 5% sodium hydroxide was boiled until the anhydride had dissolved completely (20 minutes). The solution was extracted with ether and acidified (to Congo) with 5% hydrochloric acid. The acid, separating in the form of monohydrate (0.18 g), is a white powder, again changing to the anhydride (VII) when heated, m.p. 163-164°.

Found %: C 65.5; H 7.5. M 352. $C_{19}H_{24}O_5 \cdot H_2O$. Calculated %: C 65.1; H 7.9. M 350.

Reduction of anhydride (VII) by the Clemmensen method. A mixture of 1.7 g anhydride (VII), 23 ml glacial acetic acid, 20 ml concentrated hydrochloric acid and 6.5 g amalgamated zinc turnings was boiled 40 hours, during which period addition was made in three portions of 9 g zinc turnings, 30 ml concentrated hydrochloric acid and 10 ml toluene. At the conclusion of the heating, the solvents were driven off and the residue was diluted with water and extracted with ether. After drying and evaporation, the ethereal solution was diluted with ligroine (1 ml). Crystals of the anhydride (X) came down on standing; they were filtered and washed with ligroine. Yield 0.9 g anhydride with m.p. 85-93°. Crystallization from ligroine gave 0.5 g pure anhydride (X) in the form of stout, transparent crystals with m.p. 94-96°.

Found %: C 75.85, 75.95; H 8.1, 8.0. $C_{19}H_{24}O_3$. Calculated %: C 76.0; H 8.05.

Dehydrogenation of anhydride (X). A mixture of 0.5 g anhydride (X), 20 ml dry benzene and 1 g 10% palladized carbon was heated in a rotating autoclave at 350-360° for 6 hours under a nitrogen pressure of about 100 atm. After filtration and removal of solvent, a viscous, brownish, fluorescent liquid was left from which crystals could not be obtained. Chromatography of the reaction product on alumina gave, on elution with ligroine, a few crystallizing fractions from which 15 mg crystals with m.p. 96-97° was isolated. They did not give a depression of melting point when mixed with a specimen of pure phenanthrene (99.5°). The picrate had m.p. 142-142.5° and likewise did not give a depression in admixture with pure phenanthrene picrate.

Preparation of trans-1-ethynyl-1-decalol (XI). 1 liter liquid ammonia was charged into a 3-liter, round-bottomed flask, fitted with mechanical stirrer and mercury seal and cooled with a mixture of solid carbon dioxide and acetone (−70°), followed gradually by 33.5 g sodium while stirring. A gentle stream of dry acetylene was passed into the dark blue solution for 5 hours until the color had completely disappeared. A solution of 100 g trans-decalol in 500 ml absolute ether was added to the resultant suspension of sodium acetylide at −60 to −70° in the course of half an hour, whereupon acetylene was passed in for another 7 hours. The temperature of the reaction mixture gradually rose to −35°, and then addition was made in small portions of 150 g dry ammonium chloride. The greater part of the ammonia was removed by free evaporation; 200 ml ether and 400 ml water were added; the ether layer was separated, and the aqueous layer was extracted 3 times with ether. The combined ether extracts were washed with 5% hydrochloric acid and dried with sodium sulfate. The product was fractionated in vacuum to give 112.8 g (96%) trans-1-ethynyl-1-decalol (XI) with b.p. 81-83° at 1 mm, n_D^{19} 1.5068. The literature [6] reports b.p. 94-96° at 1 mm, n_D^{20} 1.5020.

Hydrogenation of trans-1-ethynyl-1-decalol (XI) to trans-1-vinyl-1-decalol (XII). 52 g trans-1-ethynyl-1-decalol (XI) was hydrogenated with palladium on calcium carbonate in 100 ml alcohol until absorption of exactly one molecule hydrogen (7.40 liters at 22° and 719 mm). Yield 49.8 g (95%) trans-1-vinyl-1-decalol (XII) with b.p. 86-88° at 1.5 mm, n_D^{21} 1.5042. The literature reports [6] b.p. 92-93° at 2 mm, n_D^{20} 1.5055.

Preparation of β-(trans-α-decalidene)-ethyl bromide (XIII). A stream of hydrogen bromide was passed at 0° for 15 minutes into a solution of 10 g trans-1-vinyl-1-decalol (XII) in 50 ml ether until the weight increase was 6.5 g. The reaction product was stirred 1 hour at 0°; the aqueous layer was separated, and the ether layer was washed 3 times with water and dried with potassium carbonate. The ether was driven off and the product fractionated in vacuum to give 13.5 g (99%) β-(trans-α-decalidene)-ethyl bromide (XIII) with b.p. 98-100° at 1 mm, n_D^{21} 1.5400, d_D^{20} 1.2180.

Found %: C 59.15, 59.2; H 7.9, 7.8; Br 32.8, 33.0. $C_{12}H_{19}Br$. Calculated %: C 59.3; H 7.9; Br 32.9.

The bromide (XIII) was subsequently not distilled but reacted as the crude product (n_D^{21} 1.5400) obtained after removal of the ether in vacuum.

Condensation of β-(trans-α-decalidene)-ethyl bromide (XIII) with 2-methyl-cyclohexanedione-1,3 (II). 29.3 g bromide (XIII) was added with stirring in the course of 15 minutes to a solution of the Na-derivative of 1-methylcyclohexanedione-1,3, prepared as described above from 9.7 g sodium, 45 ml anhydrous methanol and 15 g 1-methylcyclohexanedione-1,3, while the temperature rose to 45°. The mixture was stirred $1^1/_2$ hours at room temperature and then boiled on a water bath until the alkaline reaction to litmus had disappeared (about 40 minutes). The condensation product crystallized in part on cooling. The methanol was taken off in a low vacuum, 50 ml water was added to the residue, and the crystals (27 g) were filtered off. Crystallization from a mixture of ligroine and n-heptane gave 20.8 g 2-methyl-2-[β-(α-decalidene-ethyl)]-cyclohexanedione-1,3 (XIV) with m.p. 73-75°. 3.2 g 2-methylcyclohexanedione-1,3 was recovered unchanged. The yield of diketone (XIV), reckoned on the 2-methylcyclohexanedione-1,3, was 78%.

Found %: C 79.25, 79.0; H 10.0, 9.85. $C_{19}H_{28}O_2$. Calculated %: C 79.1; H 9.8.

Cyclization of diketone (XIV). A well-stirred mixture of 2 g diketone (XIV) and 0.5 g phosphorus pentoxide was heated in vacuum (30 mm) at 120-130° for 40 minutes. During this period the refractive index of the mixture rose from n_D^{22} 1.5260 to n_D^{22} 1.5660. The reaction mixture was cooled, treated with saturated sodium carbonate solution and extracted with ether. The ethereal extract was washed with water and dried with magnesium sulfate. The residue was heated 15 minutes at 100° in vacuum (1 mm). The residue was dissolved in 1 ml n-heptane and left overnight at -70°. Yield 200 mg (11%) 13-methyl-$\Delta^{8,14(15)}$-allocardochrysadienone-17a (XV), with m.p. 84-88°. Crystallization from ligroine gave 150 mg pure ketone (XV) with m.p. 93-95°.

Found %: C 84.1, 84.3; H 9.4, 9.7. $C_{19}H_{26}O$. Calculated %: C 84.4; H 9.7.
Dinitrophenylhydrazone: m.p. 233-235° (from dioxane).
Found %: N 11.6, 11.65. $C_{25}H_{30}O_4N_4$. Calculated %: N 12.4.

Distillation of the mother liquors after crystallization from heptane (total of 9 g from several experiments) gave 1.5 g viscous, non-crystallizing oil with b.p. 167-169° at 1 mm, n_D^{20} 1.5590, consisting evidently of a mixtrue of stereoisomers of ketone (XV).

Found %: C 84.3, 84.4; H 9.8, 9.65. $C_{19}H_{26}O$. Calculated %: C 84.4; H 9.7.

From 1.1 g of the liquid mixture of ketones was obtained 1 g of a mixture of dinitrophenylhydrazones with m.p. 179-184°, from which (by crystallization) were isolated 0.5 g of the dinitrophenylhydrazone of the crystalline ketone (XV) (m.p. 233-235°) and 50 mg of the isomeric dinitrophenylhydrazone with m.p. 204-206° (from dioxane).

Reduction of ketone (XV) by the Kizhner method and dehydrogenation of the resultant hydrocarbon. A mixture of 0.5 g liquid mixture of stereoisomers of ketone (XV), 5 ml alcohol, 3 ml triethylene glycol and 0.4 g hydrazine hydrate was boiled 2 hours on a water vath. A solution of sodium glycolate (from 0.4 g sodium and 10 ml triethylene glycol) was then added and the temperature was raised to 190° in the course of 2 hours; at the same time, the easily volatile products were distilled off, after which the mixture was heated another 8 hours at 200-225°. All operations were conducted in a stream of nitrogen. The reaction mass was treated with 20 ml water and extracted with ether. The ether extract was washed twice with 10% hydrochloric acid and with water and dried with calcium chloride. After the ether had been driven off, 15 ml dry benzene was added and the latter slowly distilled off to remove the traces of moisture. The residue (0.3 g, n_D^{20} 1.5330) was dissolved in 5 ml dry benzene and 0.3 g 10% Pd on carbon was added and the mixture heated in a metal ampoule in a nitrogen atmosphere for 7 hours at 360-370°. After filtration and removal of solvent, the residue partly crystallized. Yield 15 mg chrysene with m.p. 245-246°, not giving a depression of melting point with an authentic specimen. The trinitrobenzoate had m.p. 185-186° and likewise did not give a depression with the trinitrobenzoate of pure chrysene.

Hydrogenation of ketone (XV). 0.4 g ketone (XV) with m.p. 93-95° in 5 ml anhydrous alcohol and 5 ml absolute ether was hydrogenated with Adams platinum. In 3 hours 36 ml H_2 (18°, 739 mm) was absorbed; hydrogenation then slowed down considerably and ceased completely after expiration of another hour (4 ml absorbed). The theoretical absorption is 36.5 ml hydrogen. After filtration and removal of solvent, a colorless, viscous, non-crystallizing oil remained (0.4 g).

Attempt to condense ketone (XV) with maleic anhydride. A solution of 200 mg ketone (XV) with m.p. 93-95° and 76 mg maleic anhydride in 6 ml benzene was heated in presence of a trace of pryogallol at 185-195° for 4 hours in a metal ampoule. After driving off the benzene, diluting with acetone and cooling, crystals (100 mg) came down and were identified as starting ketone, melting after recrystallization at 93-95° and not giving a depression in admixture with the original substance. On condensing ketone (XV) with maleic anhydride at 200-205°, neither the original crystalline ketone (XV) nor the corresponding adduct was isolated.

Preparation of 2-methylcyclopentanetrione-1,3,4. A cooled mixture of 36 g methyl ethyl ketone and 160 g diethyl oxalate was added with stirring in the course of 15 minutes to a solution of sodium ethoxide (from 23 g sodium in 315 ml anhydrous alcohol) cooled to -10°. The temperature was then gradually raised to room temperature and the mixture boiled 30 minutes on a water bath. 55 ml sulfuric acid (1:1) was added to the reaction mixture with stirring and cooling, and the separated sodium sulfate was filtered and washed with alcohol. The filtrate was evaporated in vacuum to a volume of 100 ml at a temperature not higher than 40°. The crystals that separated on cooling were filtered, washed a few times with iced water and dried in the air. Crystallization from ethyl acetate in presence of active carbon gave 41 g (36%) ethyl ester of 2-methylcyclopentanetrione-1,3,4-glyoxylic-5-acid with m.p. 160-161° [3].

A mixture of 20 g of the prepared ketoester, 100 ml concentrated hydrochloric acid and 20 ml water was heated with stirring on a boiling water bath for 45 minutes. The mixture was cooled and thoroughly extracted with ether (10 times). The ether was driven off and 15 ml water was added to the residue. The latter was heated until dissolved and left to crystallize. Yield 14 g crystals with m.p. 58-62°, which, after two crystallizations from water, gave 11 g (77%) monohydrate of 2-methylcyclopentanetrione-1,3,4 with m.p. 76-77° [3].

Preparation of 2-methylcyclopentanedione-1,3 (XVII). 16 g monohydrate of 2-methylcyclopentanetrione-1,3,4 in 125 ml anhydrous alcohol was hydrogenated in presence of Adams catalyst (210 mg PtO_2). During 5 hours 4.7 liters hydrogen was absorbed as against the theoretical requirement of 5.7 liters. The catalyst was filtered off, the alcohol driven off in a low vacuum, and the residue dissolved in 25 ml hot water and left to crystallize. 1.85 g (15%) 2-methylcyclopentanedione-1,3 (XVII) came down. M.p. 183-192°. Two crystallizations gave 1.6 g pure diketone (XVII) with m.p. 210-212° [3].

From the mother liquor was isolated 4.8 g 2-methylcyclopentanol-4-dione-1,3 with m.p. 165-168°.

Condensation of β-(trans-α-decalidene)-ethyl bromide (XIII) with 2-methylcyclopentanedione-1,3 (XVII). 1.8 g 2-methylcyclopentanedione-1,3 was added with stirring to a solution of sodium methoxide (from 0.4 g sodium and 8 ml anhydrous methanol). The mixture was boiled 5 minutes and cooled, and 4 g freshly prepared bromide (XIII) was introduced. The reaction mass was stirred at 20° for 1 hour and boiled another hour on a water bath. The methanol was driven off in a low vacuum; after addition of 20 ml water, the residue was extracted with ether. The ethereal extract was washed 3 times with saturated sodium carbonate solution and then with water, and dried with sodium sulfate. The ether was driven off and 1 ml hexane was added to the residue which was then left to crystallize at -70°. Yield 1.8 g (41%) 2-methyl-2-[β-(α-decalidene-ethyl)]-cyclopentanedione-1,3 (XVIII) with m.p. 55-56°; 2 crystallizations from hexane gave 1.5 g pure diketone (XVIII) with m.p. 60-61°.

Found %: C 79.15, 79.1; H 9.9, 9.5. $C_{18}H_{26}O_2$. Calculated %: C 78.8; H 9.55.

Cyclization of diketone (XVIII). A mixture of 1.5 g diketone (XVIII) and 0.5 g phosphorus pentoxide was heated in vacuum (25 mm) at 125-135° for 2 hours. During this period the refractive index of the mixture rose from 1.5230 to 1.5540. The reaction mixture was treated with sodium carbonate solution, extracted 3 times with ether and dried with magnesium sulfate. The residue after removal of the ether did not crystallize and was therefore twice distilled in vacuum. Yield 150 mg (12%) unpurified 13-methyl-$\Delta^{8,14(15)}$-allosteradienone-17 (XIX) with b.p. 158-160° at 1 mm, n_D^{24} 1.5560.

Found %: C 85.3, 85.4; H 9.8, 9.6. $C_{18}H_{24}O$. Calculated %: C 84.3; H 9.4.

Dinitrophenylhydrazone: m.p. 186° (from alcohol-chloroform mixture).

Found %: N 12.6, 12.8. $C_{24}H_{28}O_4N_4$. Calculated %: N 12.8.

Preparation of 1-acetyl-6-methoxynaphthalene (XXIII). The starting 6-methoxynaphthoic acid with m.p. 178.5-179° was obtained in 9% yield from furoic acid by the known method [7]. A solution of 10 g 6-methoxynaphthoic acid in 40 ml benzene was mixed with 18 ml thionyl chloride; 5 drops pyridine was added and the mixture left at room temperature for 6 hours with occasional shaking. The solvent and excess thionyl chloride were driven off in low vacuum and the residual 6-methoxynaphthoyl chloride was used without further purification for preparation of ketone (XXIII). 11.2 g anhydrous cadmium chloride was added in small portions to an ice-cooled solution of methylmagnesium bromide, prepared from 2.25 g magnesium, 12 g methyl bromide and 50 ml absolute ether. The suspension was stirred 3 1/2 hours at 20°, after which the ether was driven off and 50 ml benzene was added; the solution of the above-described 6-methoxynaphthoyl chloride in 50 ml benzene was then introduced and the mixture boiled 2 1/2 hours. The cooled reaction mixture was treated with ice and then with 10% hydrochloric acid (50 ml). The benzene solution was separated, the aqueous layer extracted with ether, and the combined extracts washed with sodium carbonate solution and dried with sodium sulfate. The solvent was removed in low vacuum. The residue crystallized after dilution with 2 ml ligroine and 1 ml methanol. Yield 7.5 g (83%) ketone (XXIII) with m.p. 58-61.5°. The pure ketone has m.p. 64-65° (from methanol).

Found %: C 77.9, 77.9; H 6.0, 6.0. $C_{13}H_{12}O_2$. Calculated %: C 78.0; H 6.0.

Bromination of 1-acetyl-6-methoxynaphthalene (XXIII). The best results were obtained with the help of dioxane dibromide. 5.3 g dioxane dibromide was added with stirring in the dark in the course of 3 hours to a solution (cooled to −8 to −9°) of 4 g 1-acetyl-6-methoxynaphthalene (XXIII) in 20 ml absolute ether. Stirring was afterwards continued for 30 minutes. The ethereal solution was then washed 3 times with water and dried with sodium sulfate. The solvent was driven off to leave a volume of 17 ml. Crystallization gave three fractions: 0.1 g with m.p. 120-126°, 2.8 g with m.p. 65-67° and 0.25 g with m.p. 66-67°. The second and third fractions of crystals were mainly 1-bromoacetyl-6-methoxynaphthalene (XXIV). After one crystallization the yield of bromoketone (XXIV) with m.p. 66-68° was 2.30 g (41%). The pure bromoketone (XXIV) has m.p. 71° (from ligroine).

Found %: Br 28.8, 28.9. $C_{13}H_{11}O_2Br$. Calculated %: Br 28.6.

Crystals with m.p. 135.5-136° (from methanol) were isolated from the first fraction and evidently consisted of 1,1-dibromoacetyl-6-methoxynaphthalene.

Found %: Br 42.8, 43.2. $C_{13}H_{10}O_2Br_2$. Calculated %: Br 44.6.

Condensation of 2-methylcyclohexanedione-1,3 (II) with 1-bromoacetyl-6-methoxynaphthalene (XXIV). To a solution of 0.3 g potassium hydroxide in 1.5 ml water was added 0.7 g of ketone (II) and the mixture stirred 5 minutes at 70°. To the resultant K-derivative of diketone (II) was added dropwise at 20° a solution of 1.5 g bromide (XXIV) in 3.5 ml dioxane and the mixture was stirred at 80-90° for 30 minutes, after which the alkaline reaction had disappeared. The reaction mass was extracted with ether, the ethereal extracts were washed with sodium carbonate solution for removal of the methylcyclohexanedione (II), dried with sodium sulfate and evaporated to a small volume. On cooling (towards the end with dry ice), 0.85 g (47%) of triketone (XXV) came down with m.p. 107-108.5°. The pure triketone (XXV) has m.p. 111-112° (from benzene).

Found %: C 74.0, 73.9; H 6.2, 6.4. $C_{20}H_{20}O_4$. Calculated %: C 74.05; H 6.2.

Attempts to cyclize triketone (XXV). Triketone (XXV) was heated in presence of 10-20% phosphorus pentoxide at 115-150° in a 30-40 mm vacuum, and also without vacuum but in acetic anhydride solution. One experiment was performed with 2 hours boiling in benzene with 10 times the amount of phosphorous pentoxide. In all cases the reaction product was a dark, viscous liquid from which a crystalline substance could not be isolated even by chromatography. In some experiments, parts of the original triketone (XXV) was recovered.

Attempts to cyclize triketone (XXI).* a) 2 g phosphorus pentoxide was added to a solution of 2 g triketone (XXI) in 20 ml anhydrous benzene, and the mixture boiled 2 hours while stirring. While cooling, the mixture was decomposed with iced water and neutralized with sodium carbonate until alkaline; the benzene layer was separated and the aqueous layer extracted with ether. Evaporation of the ether-benzene solution and crystallization gave 1.4 g original triketone with m.p. 121-124°. Acidification of the aqueous alkaline solution gave 0.15 g methyldihydroresorcinol, m.p. 200°. b) A mixture of 1 g triketone (XXI) and 0.2 g phosphorus pentoxide was heated 1 hour at 120°. Working up in the usual manner gave 0.2 g original triketone. The residue was a dark, uncrystallizable oil. Increase of temperature to 140° led to complete resinification. c) To a solution of 1 g triketone (XXI) in 10 ml anhydrous benzene was added 1 ml tin chloride and the mixture was boiled 1 hour. Suitable treatment led only to a dark resin. Attempts to employ other cyclizing agents likewise did not give the desired results. Thus, with phosphoric acid, sp.gr. 1.75 (130-140°, 3 hours) and with 80% sulfuric acid (at −20°) the reaction did not go. Only resins were obtained with phosphoric acid sp.gr. 1.78 (160°, 3 hours), phosphoric acid (20-65°), or 80% sulfuric acid (80°, 10 minutes). Acetic anhydride (120-130°, 4 minutes) brings about ring closure to the previously described unsaturated acid $C_{15}H_{16}O_3$.

SUMMARY

Condensations were effected of 2-methylcyclohexanedione-1,3 (II) with β-cyclohexylideneethyl bromide (I), β-(trans-α-decalidene)-ethyl bromide (XIII) and 1-bromoacetyl-6-methoxynaphthalene (XXIV); also condensation of 2-methylcyclopentanedione-1,3 (XVII) with β-(trans-α-decalidene)-ethyl bromide (XIII). The

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*Experimental work by M. S. Burmistrova.

products were 2,2-disubstituted cyclic 1,3-diketones (III), (XIV), (XXV) and (XVIII). Diketones (III), (XIV) and (XVIII) cyclize when heated with phosphorus pentoxide in vacuum to give the heteroannulised polycyclic dienones (IV), (XV) and (XIX) which are based on the hydrogenated skeletons of phenanthrene, chrysene and cyclopentanophenanthrene. Triketone (XXV) does not cyclize under these conditions; the similarly constituted triketone (XXI) also does not cyclize in presence of various acidic agents.

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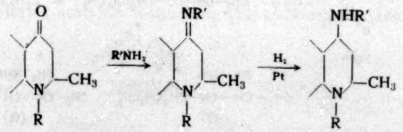
HETEROCYCLIC COMPOUNDS

38. SYNTHETIC SPASMOLYTICS. PREPARATION OF 4-AMINOPIPERIDINES BY REDUCTIVE AMINATION OF 4-PIPERIDONES

I. N. Nazarov and E. T. Golovin

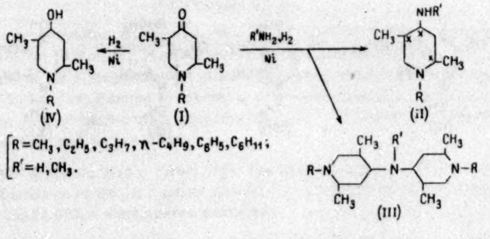
In previous communications [1,2] we described the preparation of a series of substituted 4-aminopiperidines by hydrogenation of the corresponding 4-iminopiperidines formed by reaction of 4-piperidones with primary amines.



4-Aminopiperidines are of pharmacological interest as substances possessing a strong spasmolytic action. The simplest and most convenient method for their preparation is reductive amination of 4-piperidones [3-6]. The existence of a large series of 4-piperidones synthesized in our laboratory made possible a systematic study of this reaction and the preparation of a series of substituted 4-aminopiperidones for pharmacological investigation.

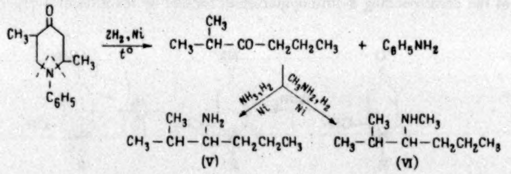
Reductive amination was carried out in a 165 ml rotating autoclave under a hydrogen pressure of 80-150 atm. at temperatures of 60 to 150° in presence of Raney nickel catalyst. Methanol was used as solvent in some experiments, but the majority of the experiments were carried out in an aqueous medium. Heating of the reaction mixture (ketone and ammonia or amine) in a hydrogen atmosphere was effected with continuous stirring to the temperature at which hydrogenation commences markedly to the accompaniment of fall of hydrogen pressure in the autoclave. After this, the temperature was held at the required level, with variations of 5-15°, until the end of the reaction, which was reflected by cessation of the fall of hydrogen pressure in the autoclave.

The course of the reductive amination of 4-piperidones and the secondary reactions observed may be represented by the following general scheme:



In reactions of 1-alkyl-2,5-dimethyl-4-piperidones (I, R = CH_3, C_2H_5, C_3H_7, n-C_4H_9), and also of 1-cyclohexyl-2,5-dimethyl-4-piperidone (I, R = C_6H_{11}) with aqueous solutions of ammonia or methylamine taken in 50 to 300% excess over the theoretically necessary amount, the corresponding primary or secondary 4-aminopiperidines (II, R = CH_3, C_2H_5, C_3H_7, n-C_4H_9, C_6H_{11}; R' = H, CH_3) are formed in 60-80% yields; by-products isolated were some dipiperidylamines (III, R = CH_3; R' = H, CH_3), and also 4-piperidols (IV, R = CH_3, C_2H_5). It was observed that the amounts of the corresponding dipiperidylamine increase with decreasing amount of ammonia or methylamine taken into reaction. Thus, in the reaction of 1,2,5-trimethyl-4-piperidone (I, R = CH_3) with an insufficient amount of ammonia (50% of theory) the predominant product was di-(1,2,5-trimethyl-4-piperidyl)-amine (III, R = CH_3; R' = H) in a yield of 84% reckoned on the reacted piperidone.

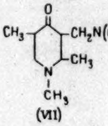
Reactions of 1-phenyl-2,5-dimethyl-4-piperidone (I, R = C_6H_5) with ammonia and methylamine gave respectively 1-phenyl-2,5-dimethyl-4-aminopiperidine (II, R = C_6H_5; R' = H) in 46.5% yield and 1-phenyl-2,5-dimethyl-4-methylaminopiperidine (II, R = C_6H_5; R' = CH_3) in 37% yield. The relatively low yields of 1-phenyl-4-aminopiperidones are due in part to the fact that a considerable amount of the original piperidone is cleaved by hydrogen to aniline and propyl-isopropyl ketone under the reaction conditions. The latter is probably also subjected to reductive amination with ammonia or methylamine with formation respectively of 2-methyl-3-aminohexane (V) and 2-methyl-3-methylaminohexane (VI), which, however, were not isolated in the pure form but were removed during working up in mixtures of low-boiling products.



The final 1-phenyl-4-aminopiperidines (II, R = C_6H_5; R' = H, CH_3) are possibly also subjected to hydrogenolysis.

It was earlier shown in our laboratory [2] that exhaustive hydrogenation of 1-phenyl-2,5-dimethyl-4-piperidone (I, R = C_6H_5) at a temperature of 200-500° and a hydrogen pressure of 90 atm. in presence of nickel catalyst resulted, apart from formation of the normal product of hydrogenation (1-cyclohexyl-2,5-dimethyl-4-piperidol), in partial cleavage of the piperidine ring; in this process, propyl-isopropyl carbinol was isolated from the neutral products of reaction. Similar cases of hydrogenolysis of 4-piperidones under the conditions of their catalytic hydrogenation have also been observed in our laboratory [7].

Reduction of 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone (VII) in presence of ammonia or methylamine gave, instead of the expected 4-amino- and 4-methylamino derivatives, 1,2,3,5-tetramethyl-4-aminopiperidine (VIII) in 40% yield and 1,2,3,5-tetramethyl-4-methylaminopiperidine (IX) in a yield of 33% respectively. In both cases a by-product (yield 20%) is 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidol (X).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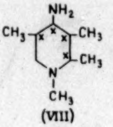
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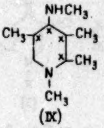
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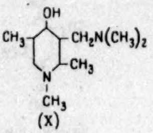

(X)

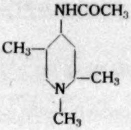
Such a reaction course is accounted for by the low stability of β-aminoketones, resulting in easy cleavage of the amine which facilitates hydrogenolysis at the side amino group.

It is interesting to note that the reductive amination of 1-alkyl-2,5,dimethyl-4-piperidones goes with facility only with ammonia and methylamine, and cannot be realized with higher aliphatic (starting from ethylamine), alicyclic and aromatic primary amines or with secondary amines under the conditions described. In these cases a secondary concurrent reaction proceeding under the same conditions begins to predominate – the reduction of the original 4-piperidone to the secondary piperidinic alcohol (IV). Thus, in the hydrogenation of 1,2,5-trimethyl-4-piperidone (I, R = CH_3) in presence of ethylamine, propylamine, isopropylamine, cyclohexylamine, and also ethanolamine, aniline, piperidine and dimethylamine, 1,2,5-trimethyl-4-piperidol (IV, R = CH_3) is formed in a yield reaching 90% in some cases, instead of the expected 4-aminopiperidines.

All the prepared 1-alkyl-2,5-dimethyl-4-aminopiperidines (II, R = CH_3, C_2H_5, C_3H_7, n-C_4H_9; R' = H, CH_3) are colorless, mobile liquids with a strong amine odor. 1-Cyclohexyl- and 1-phenyl-4-aminopiperidines (II, R = = C_6H_5, C_6H_{11}; R' = H, CH_3) are colorless, viscous liquids possessing a faint odor of bases. 4-Aminopiperidines do not alter when kept. In the air they readily form carbonates which deposit in solid form on the walls of vessels. The isolated dipiperidylamines (III, R = CH_3; R' = H, CH_3) are high-boiling, slightly mobile yellow liquids.

Crystalline hydrochlorides and picrates were prepared for characterization of all the synthesized 4-aminopiperidines and dipiperidylamines.

Reaction of acetic anhydride with some 4-aminopiperidines (II, R = CH_3, C_2H_5; R' = H) gave crystalline acetyl derivatives: 1,2,5-trimethyl-4-acetylaminopiperidine (XI) and 1-ethyl-2,5-dimethyl-4-acetylaminopiperidine (XII).



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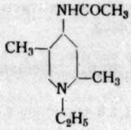

(XII)

Due to the presence of asymmetric carbon atoms in the molecule of 4-aminopiperidines (marked with crosses in the formulas), the existence of several diastereoisomers is possible. Consideration of the stereochemistry of the compounds is hindered, however, by the fact that their crystalline derivatives break down below their melting point.

The 4-aminopiperidines and dipiperidylamines were subjected to pharmacological examination in the form of hydrochlorides. Preliminary results indicate a well-marked depressive action with very low toxicity. It was also observed that toxicity and ability to lower blood pressure are both intensified by increasing weight of the radicals bound to the nitrogen atom of the piperidine ring.

EXPERIMENTAL

1,2,5-Trimethyl-4-aminopiperidine (II, R = CH_3; R' = H). A mixture of 42.5 g 1,2,5-trimethyl-4-piperidone (I, R = CH_3) (b.p. 78-81° at 14 mm, n_D^{20} 1.4600) and 30 ml 25% aqueous ammonia was hydrogenated in a 165 ml autoclave in presence of 1.5 g nickel catalyst under a hydrogen pressure of 80 atm. Reaction temperature 60-75°, duration 2 hours. The base was isolated by saturation with caustic alkali solution in presence of ether and extracted 3 times with ether. The combined ether extracts were dried with potassium carbonate. After driving off the ether, the residue was fractionated in vacuum.

1st fraction, b.p. 67-68° at 9 mm, 32.8 g (yield 77%); 2nd fraction, b.p. 85-87° at 9 mm, 3.5 g (yield 8%); resinous residue 2.6 g. Redistillation of the 1st fraction gave 31.8 g 1,2,5-trimethyl-4-aminopiperidine in the form of a colorless, mobile liquid with a weak ammoniacal odor:

B.p. 51-52° at 5 mm (47-47.5° at 3 mm), n_D^{20} 1.4678, d_4^{20} 0.8938, MR_D 44.22; calc. 44.37.
Found %: N 19.80, 19.95. $C_8H_{18}N_2$. Calculated %: N 19.70.

The 2nd fraction is 1,2,5-trimethyl-4-piperidol (IV, R = CH_3).

Found %: N 9.81. $C_8H_{17}ON$. Calculated %: N 9.78.

The dipicrate of 1,2,5-trimethyl-4-aminopiperidine was obtained by mixing hot alcoholic solutions of the base and picric acid. The precipitate was recrystallized from 50% alcohol and then melted at 228° (with decomposition).

Found %: N 18.49, 18.54. $C_{20}H_{24}O_{14}N_8$. Calculated %: N 18.66.

The dihydrochloride of 1,2,5-trimethyl-4-aminopiperidine was obtained by passing dry hydrogen chloride into an ethereal solution of the base. The precipitate was collected and washed on the filter with absolute ether; after recrystallization from alcohol-methanol mixture it melted at 321° (with decomposition). The dihydrochloride is readily soluble in water and methanol, moderately soluble in ethyl alcohol, insoluble in acetone.

Found %: N 12.61, 12.86; Cl 32.41, 32.77. $C_8H_{20}N_2Cl_2$. Calculated %: N 13.02; Cl 32.96.

Di-(1,2,5-trimethyl-4-piperidyl)-amine (III, R = CH_3; R' = H). 28.2 g (0.2 mole) 1,2,5-trimethyl-4-piperidone, 30 ml methanol and 1.5 g Raney nickel were charged into an autoclave. Gaseous ammonia was then pressed in under a pressure of 8 atm and hydrogen under a pressure of 140 atm (25°). Reaction temperature 74-80°, duration $1\frac{1}{2}$ hours. Pressure at end of reaction 115 atm (25°), hydrogen absorption 2,380 ml (0.11 mole). The catalyst was filtered off, and after removal of the methanol the residue was fractionated in vacuum. 9.4 g original piperidone (b.p. 55-59° at 4 mm, n_D^{20} 1.4630) was recovered unchanged and 15 g di-(1,2,5-trimethyl-4-piperidyl)-amine was obtained in the form of a viscous, slightly mobile yellow liquid with b.p. 135-141° at 4 mm. Resinous residue 2 g. The yield on the reacted piperidone is 84%. Redistillation gave 11.5 g product with b.p. 137-139° at 4 mm, n_D^{20} 1.4902.

Found %: N 16.00, 15.74. $C_{15}H_{33}N_3$. Calculated %: N 15.71.

The trihydrochloride of di-(1,2,5-trimethyl-4-piperidyl)-amine melted at 296° (with decomposition) after recrystallization from alcohol-methanol mixture.

Found %: Cl 28.42, 27.97. $C_{16}H_{36}N_3Cl_3$. Calculated %: Cl 28.23.

1,2,5-Trimethyl-4-methylaminopiperidine (II, R = R' = CH_3). a) A mixture of 28.2 g (0.2 mole) 1,2,5-trimethyl-4-piperidone (b.p. 66-68° at 7 mm, n_D^{19} 1.4605) and 44 ml 30% aqueous methylamine solution was hydrogenated, in presence of 1.5 g Raney nickel, at an initial hydrogen pressure of 149 atm (22°). Reaction temperature 65-69°, duration $2\frac{1}{2}$ hours. Final pressure 100 atm (22°); hydrogen uptake 4,080 ml (0.18 mole). The base was salted out with potassium carbonate, extracted with ether and dried with sodium sulfate. After removal of the ether, the reaction product was fractionated in vacuum to give 14.4 g (yield 46%) of 1,2,5-trimethyl-4-methylaminopiperidine [1]:

B.p. 47.5-48° at 3 mm, n_D^{22} 1.4695, d_4^{22} 0.8895, MR_D 48.97; calc. 49.10.
Found %: N 18.16, 18.00. $C_9H_{20}N_2$. Calculated %: N 17.93.

In addition, 6 g (yield 21%) 1,2,5-trimethyl-4-piperidol with b.p. 80-82° at 3 mm, n_D^{22} 1.4746 was obtained; also 4.8 g (yield 17%) of di-(1,2,5-trimethyl-4-piperidyl)-methylamine with b.p. 137-140° at 3 mm, n_D^{22} 1.4910. After fractionation, 2 g resinous residue remained.

The dipicrate of 1,2,5-trimethyl-4-methylaminopiperidine melts at 239° (with decomposition) after recrystallization from 50% alcohol.

Found %: N 18.26, 18.30. $C_{21}H_{26}O_{14}N_8$. Calculated %: N 18.24.

The dihydrochloride of 1,2,5-trimethyl-4-methylaminopiperidine melts at 315° (with decomposition) after recrystallization from alcohol-methanol mixture.

Found %: N 12.46, 12.19; Cl 30.91, 30.60. $C_9H_{22}N_2Cl_2$. Calculated %: N 12.22; Cl 30.94.

b) Substances taken into reaction were 30 g 1,2,5-trimethyl-4-piperidone, 45 ml 20% methylamine solution in methanol and 1.5 g Raney nickel. Hydrogen pressure 100 atm, reaction temperature 90-100°, duration 1 hour. After removal of the catalyst and distillation of the methanol, the residue was fractionated in vacuum to give 18.6 g (yield 56%) of the above-described 1,2,5-trimethyl-4-methylaminopiperidine with b.p. 84-86° at 11 mm, n_D^{21} 1.4710 and 8.8 g (yield 29%) 1,2,5-trimethyl-4-piperidol with b.p. 94-98° at 11 mm, n_D^{22} 1.4758.

Di-(1,2,5-trimethyl-4-piperidyl)-methylamine (III, R = R' = CH_3). A mixture of 28.2 g (0.2 mole) 1,2,5-trimethyl-4-piperidone and 33 ml 30% aqueous methylamine solution was hydrogenated, in presence of 1.5 g Raney nickel, under an initial hydrogen pressure of 157 atm (22°). Reaction temperature 70-85°, duration 2 hours. At the end of the experiment the pressure had fallen to 117 atm (22°) and 3,700 ml hydrogen (0.165 mole) had been absorbed. The mixture was worked up in the usual manner. Vacuum fractionation of the reaction product gave 12.2 g (yield 39%) 1,2,5-trimethyl-4-methylaminopiperidine with b.p. 50-52° at 4 mm, n_D^{23} 1.4705, 7.5 g (yield 26%) 1,2,5-trimethyl-4-piperidol with b.p. 82-84° at 4 mm, n_D^{20} 1.4770, and 6.4 g (yield 23%) di-(1,2,5-trimethyl-4-piperidyl)-methylamine with b.p. 137-140° at 3 mm, n_D^{20} 1.4913.

Found %: N 15.06, 15.28. $C_{17}H_{35}N_3$. Calculated %: N 14.93.

The trihydrochloride of di-(1,2,5-trimethyl-4-piperidyl)-methylamine melted at 308° (with decomposition) after recrystallization from alcohol-methanol mixture.

Found %: Cl 27.07. $C_{17}H_{38}N_3Cl_3$. Calculated %: Cl 27.21.

Reduction of 1,2,5-trimethyl-4-piperidone (I, R = CH_3) in presence of ethylamine. A mixture of 28.2 g 1,2,5-trimethyl-4-piperidone and 18 g ethylamine, dissolved in 18 ml water, was hydrogenated in presence of 1.5 g Raney nickel under an initial hydrogen pressure of 150 atm. Reaction temperature 70-73°, duration 2½ hours. The base was salted out with potassium carbonate, extracted with ether, dried with sodium sulfate and (after removal of the ether) fractionated in vacuum: 1st fraction, b.p. 48-65° at 4 mm, n_D^{21} 1.4667, 4 g; 2nd fraction, b.p. 79-82° at 4 mm, n_D^{21} 1.4752, 21 g.

The 2nd fraction is the previously described [8] 1,2,5-trimethyl-4-piperidol (IV, R = CH_3) (yield 73.5%); a colorless, viscous liquid.

Found %: N 9.83, 9.53. $C_8H_{17}ON$. Calculated %: N 9.78.

Reductive amination of 1,2,5-trimethyl-4-piperidone cannot be realized with ethylamine and propylamine, either under mild or drastic conditions of temperature and pressure both in alcoholic solution and without a solvent. In all cases, smaller or larger amounts of 1,2,5-trimethyl-4-piperidol are formed. Preheating of the starting components before introduction of hydrogen leads to formation of the corresponding imino compounds and a complex mixture of close-boiling substances is obtained.

Other amines behave similarly in this reaction. Reduction of 1,2,5-trimethyl-4-piperidone in presence of aqueous solutions of ethanolamine, isopropylamine and dimethylamine gave respectively 77, 86.5 and 90% yields of 1,2,5-trimethyl-4-piperidol. Reduction of 1,2,5-trimethyl-4-piperidone in an aqueous or alcoholic medium in presence of aniline, cyclohexylamine and piperidine also goes in the direction of formation of only 1,2,5-trimethyl-4-piperidol and the corresponding aminopiperidines are not formed at all under the chosen conditions.

1-Ethyl-2,5-dimethyl-4-aminopiperidine (II, R = C_2H_5; R' = H). 10 g 1-ethyl-2,5-dimethyl-4-piperidone (I, R = C_2H_5) (b.p. 76-78° at 6 mm, n_D^{20} 1.4630), 15 ml 25% aqueous ammonia and 1.5 g Raney nickel were taken into reaction. Initial hydrogen pressure 122 atm (22°), reaction temperature 65-75°, duration 1 hour. Pressure at end of experiment 109 atm (22°), hydrogen absorption 1,630 ml. The base was salted out with potassium carbonate, extracted with ether, dried with sodium sulfate and (after the ether had been driven off) fractionated in vacuum: 1st fraction, b.p. 48-49° at 2.5 mm, 6.1 g (61%); 2nd fraction, b.p. 69.5-70° at 1.5 mm, 2.0 g (20%); 3rd fraction, b.p. 146-149° at 1.5 mm, 1.0 g.

The 1st fraction is 1-ethyl-2,5-dimethyl-4-aminopiperidine:

n_D^{20} 1.4687, d_4^{20} 0.8886, MR_D 48.95; calc. 48.92.
Found %: N 17.93, 17.80. $C_9H_{20}N_2$. Calculated %: N 17.93.

Dipicrate of 1-ethyl-2,5-dimethyl-4-aminopiperidine melted at 215° (with decomposition) after recrystallization from aqueous alcohol. Fine, lustrous, light yellow grains.

Found %: N 18.18, 18.15. $C_{21}H_{26}O_{14}N_8$. Calculated %: N 18.24.

The 2nd fraction is 1-ethyl-2,5-dimethyl-4-piperidol (IV, R = C_2H_5); a colorless, viscous liquid with a faint amine odor:

n_D^{20} 1.4763, d_4^{20} 0.9525, MR_D 46.59; calc. 47.03.
Found %: N 9.32, 9.17. $C_9H_{19}ON$. Calculated %: N 8.91.

1-Ethyl-2,5-dimethyl-4-methylaminopiperidine (II, R = C_2H_5; R' = CH_3). 12.5 g 1-ethyl-2,5-dimethyl-4-piperidone, 25 ml aqueous methylamine solution and 1.5 g Raney nickel were taken into reaction. Hydrogen was pressed in under a pressure of 117 atm; reaction temperature 60-75°, duration 1 hour. Final hydrogen pressure 102 atm (22°), hydrogen absorbed 1,720 ml. The mixture was worked up as in the preceding experiment. Yield 5.5 g (40%) 1-ethyl-2,5-dimethyl-4-methylaminopiperidine:

B.p. 77-78° at 10 mm, n_D^{20} 1.4706, d_4^{20} 0.8912, MR_D 53.37; calc. 53.72.
Found %: N 16.57, 16.01. $C_{10}H_{22}N_2$. Calculated %: N 16.45.

In addition, 2.6 g (yield 20.5%) of the above-described 1-ethyl-2,5-dimethyl-4-piperidol was isolated; b.p. 70-71° at 1.5 mm, n_D^{17} 1.4787.

The dipicrate of 1-ethyl-2,5-dimethyl-4-methylaminopiperidine melted at 222-223° (with decomposition) after recrystallization from aqueous alcohol.

Found %: N 17.62, 17.49. $C_{22}H_{28}O_{14}N_8$. Calculated %: N 17.83.

The dihydrochloride of 1-ethyl-2,5-dimethyl-4-methylaminopiperidine melted at 294° (with decomposition) after recrystallization from alcohol-acetone mixture.

Found %: N 11.50, 11.38; Cl 28.95. $C_{10}H_{24}N_2Cl_2$. Calculated %: N 11.52; Cl 29.16.

1-Propyl-2,5-dimethyl-4-aminopiperidine (II, R = C_3H_7; R' = H). 17 g (0.1 mole) 1-propyl-2,5-dimethyl-4-piperidone (I, R = C_3H_7) (b.p. 88-90° at 8 mm, n_D^{20} 1.4602), 30 ml 25% aqueous ammonia and 1.5 g Raney nickel were charged into an autoclave. Gaseous ammonia was then pressed in at a pressure of 12 atm and hydrogen under a pressure of 143 atm (22°). Reaction temperature 60-66°, duration 3 hours. The pressure fell to 121 atm (22°), and 2,360 ml (0.1 mole) hydrogen was absorbed. The mixture was worked up in the usual manner to give 13.7 g (80%) 1-propyl-2,5-dimethyl-4-aminopiperidine.

B.p. 65-66° at 3 mm, n_D^{20} 1.4672, d_4^{20} 0.8904, MR_D 53.09; calc. 53.54.
Found %: N 16.90, 16.65. $C_{10}H_{22}N_2$. Calculated %: N 16.45.

The dipicrate of 1-propyl-2,5-dimethyl-4-aminopiperidine melted at 218° (with decomposition) after recrystallization from aqueous alcohol. Yellow, lustrous needles.

Found %: N 17.95, 17.97. $C_{22}H_{28}O_{14}N_8$. Calculated %: N 17.83.

The dihydrochloride of 1-propyl-2,5-dimethyl-4-aminopiperidine melted at 150°(with decomposition) after recrystallization from alcohol-acetone mixture.

Found %: N 11.16, 11.35; Cl 28.83. $C_{10}H_{24}N_2Cl_2$. Calculated %: N 11.52; Cl 29.16.

1-Propyl-2,5-dimethyl-4-methylaminopiperidine (II, R = C_3H_7; R' = CH_3). 10 g 1-propyl-2,5-dimethyl-4-piperidone, 23 ml 25% aqueous methylamine solution and 1.5 g Raney nickel were taken into reaction. Initial hydrogen pressure 145 atm (22°), reaction temperature 60-67°, duration 2 hours. Final pressure 134 atm (22°), hydrogen absorption 1,320 ml. Yield 7.1 g (65%) 1-propyl-2,5-dimethyl-4-methylaminopiperidine:

B.p. 63-64° at 2 mm, n_D^{22} 1.4680, d_4^{22} 0.8780, MR_D 58.36; calc. 58.34.
Found %: N 15.39, 15.08. $C_{11}H_{24}N_2$. Calculated %: N 15.20.

The dipicrate of 1-propyl-2,5-dimethyl-4-methylaminopiperidine melted at 213° (with decomposition) after recrystallization from aqueous alcohol. Yellow, lustrous needles.

Found %: N 17.00, 17.39. $C_{23}H_{30}O_{14}N_8$. Calculated %: N 17.44.

The dihydrochloride of 1-propyl-2,5-dimethyl-4-methylaminopiperidine melted at 164° (with decomposition) after recrystallization from alcohol-acetone mixture.

Found %: N 11.03, 10.72; Cl 27.38. $C_{11}H_{26}N_2Cl_2$. Calculated %: N 10.89; Cl 27.57.

1-n-Butyl-2,5-dimethyl-4-aminopiperidine (II, R = n-C_4H_9; R' = H). 9.2 g (0.05 mole) 1-n-butyl-2,5-dimethyl-4-piperidone (I, R = n-C_4H_9) (b.p. 75-78° at 2 mm, n_D^{19} 1.4607), 15 ml 25% aqueous ammonia and 1.5 g Raney nickel were taken into reaction. Ammonia was then pressed into the autoclave at 12 atm pressure. The mixture was hydrogenated at an initial pressure of 145 atm hydrogen (22°); reaction temperature 70-75°, duration 4 hours. Final pressure 137 atm (22°), hydrogen absorption 1,030 ml (0.046 mole). After working up in the usual manner, fractionation in vacuum gave 5.8 g (yield 63%) 1-n-butyl-2,5-dimethyl-4-aminopiperidine:

B.p. 76-77° at 2 mm, n_D^{20} 1.4680, d_4^{20} 0.8828, MR_D 58.04; calc. 58.16.
Found %: N 14.98, 15.00. $C_{11}H_{24}N_2$. Calculated %: N 15.20.

The dipicrate of 1-n-butyl-2,5-dimethyl-4-aminopiperidine melted at 238° (with decomposition) after recrystallization from aqueous alcohol.

Found %: N 17.32. $C_{23}H_{30}O_{14}N_8$. Calculated %: N 17.44.

The dihydrochloride of 1-n-butyl-2,5-dimethyl-4-aminopiperidine melted at 277° (with decomposition) after recrystallization from alcohol-acetone mixture.

Found %: N 10.73, 10.94; Cl 27.27. $C_{22}H_{26}N_2Cl_2$. Calculated %: N 10.89; Cl 27.57.

1-n-Butyl-2,5-dimethyl-4-methylaminopiperidine (II, R = n-C_4H_9; R' = CH_3). 10 g (0.055 mole) 1-n-butyl-2,5-dimethyl-4-piperidone, 20 ml 25% aqueous methylamine solution and 1.5 g Raney nickel were taken into reaction. Initial hydrogen pressure 142 atm (23°), reaction temperature 73-77°, duration 4 hours. Final pressure 133 atm (23°), hydrogen absorption 1,120 ml (0.05 mole). Yield 6.4 g (59%) of 1-n-butyl-2,5-dimethyl-4-methylaminopiperidine.

B.p. 81.5-82° at 3 mm, n_D^{20} 1.4682, d_4^{20} 0.8848, MR_D 62.34; calc. 62.96.
Found %: N 14.09, 14.21. $C_{12}H_{26}N_2$. Calculated %: N 14.12.

The dipicrate of 1-n-butyl-2,5-dimethyl-4-methylaminopiperidine melted at 232° (with decomposition) after recrystallization from aqueous alcohol.

Found %: N 17.36, 17.13. $C_{24}H_{32}O_{14}N_8$. Calculated %: N 17.07.

The dihydrochloride of 1-n-butyl-2,5-dimethyl-4-methylaminopiperidine melted at 274° (with decomposition) after recrystallization from alcohol-acetone.

Found %: N 10.27, 10.55; Cl 26.24. $C_{12}H_{28}N_2Cl_2$. Calculated %: N 10.33; Cl 26.14.

1-Cyclohexyl-2,5-dimethyl-4-aminopiperidine (II, R = C_6H_{11}; R' = H). 5.2 g 1-cyclohexyl-2,5-dimethyl-4-piperidone (I, R = C_6H_{11}) (b.p. 108-113° at 3.5 mm, m.p. 73-74°) dissolved in 20 ml methanol and 8 ml 25% aqueous ammonia were hydrogenated, in presence of 1 g Raney nickel under an initial hydrogen pressure of 100 atm (20°), while heating to 140° for 2 hours. The pressure fell to 95 atm (20°). After appropriate treatment, fractionation in vacuum gave 3.8 g (yield 73%) 1-cyclohexyl-2,5-dimethyl-4-aminopiperidine in the form of a viscous, colorless liquid.

B.p. 117-122° at 2.5 mm, n_D^{20} 1.5015, d_4^{20} 0.9565, MR_D 64.85; calc. 65.20.
Found %: N 13.16, 13.05. $C_{13}H_{26}N_2$. Calculated %: N 13.32.

The dipicrate of 1-cyclohexyl-2,5-dimethyl-4-aminopiperidine melted at 226° (with decomposition) after recrystallization from alcohol-acetone.

Found %: N 16.55, 16.92. $C_{25}H_{32}O_{14}N_8$. Calculated %: N 16.76.

1-Phenyl-2,5-dimethyl-4-aminopiperidine (II, R = C_6H_5; R' = H). a) A mixture of 20 g (0.01 mole) 1-phenyl-2,5-dimethyl-4-piperidone (I, R = C_6H_5) (b.p. 116-119° at 1 mm, n_D^{21} 1.5519), 23 ml 25% aqueous ammonia and 6 ml ethanol was hydrogenated, in presence of 2 g Raney nickel, under an initial hydrogen pressure of 115 atm (22°) with heating to 170° for 3 hours. At the close of the experiment the pressure had fallen to 82 atm (22°), and 3,450 ml hydrogen (0.154 mole) had been taken up. The base was salted out with sodium carbonate, extracted with ether, dried with sodium sulfate and (after removal of the ether) fractionated in vacuum: 1st fraction, b.p. 70° at 11 mm, n_D^{20} 1.5745, 7.3 g; 2nd fraction, b.p. 114-116° at 1 mm, n_D^{20} 1.5573, 8.7 g; 3rd fraction, b.p. 125-128° at 1 mm, n_D^{20} 1.5612, 1.0 g; resinous residue 2 g.

The 1st fraction is aniline, b.p. 181-182° at 749 mm, n_D^{20} 1.5824; the hydrochloride melted at 196° (from alcohol-acetone); the picrate melted at 182-183° (with decomposition); neither gave a depression with authentic specimens.

The 2nd fraction is 1-phenyl-2,5-dimethyl-4-aminopiperidine [2] (yield 43.5%); a viscous, colorless liquid with a weak amine odor.

Found %: N 13.45, 13.46. $C_{13}H_{20}N_2$. Calculated %: N 13.71.

The dipicrate of 1-phenyl-2,5-dimethyl-4-aminopiperidine melted at 175-176° (with decomposition) after recrystallization from alcohol-acetone.

Found %: N 16.83, 16.85. $C_{25}H_{26}O_{14}N_8$. Calculated %: N 16.91.

b) 20 g 1-phenyl-2,5-dimethyl-4-piperidone, 23 ml 25% aqueous ammonia, 20 ml methanol and 2 g Raney nickel were taken into reaction. Initial hydrogen pressure 154 atm (20°), reaction temperature 90-100°, duration 1 hour. Final pressure 123 atm (20°), hydrogen absorption 2,890 ml (0.13 mole). The mixture was worked up as in the preceding experiment. Vacuum fractionation gave: 1st fraction, b.p. 74° at 13 mm, n_D^{20} 1.5813, 3.4 g; 2nd fraction, b.p. 114-117° at 1 mm, n_D^{20} 1.5574, 9.3 g; 3rd fraction, b.p. 125-129° at 1 mm, n_D^{20} 1.5613, 3.8 g.

The 1st fraction is aniline; the 2nd fraction is 1-phenyl-2,5-dimethyl-4-aminopiperidine (yield 56.5%); the 3rd fraction is a viscous, slightly mobile, yellowish liquid with a weak basic odor.

1-Phenyl-2,5-dimethyl-4-methylaminopiperidine (II, R = C_6H_5; R' = CH_3). A mixture of 20 g (0.1 mole) 1-phenyl-2,5-dimethyl-4-piperidone, 30 ml 25% aqueous methylamine and 20 ml methanol was hydrogenated, in presence of 2 g Raney nickel, under an initial hydrogen pressure of 112 atm (21°). Reaction temperature 110-120°, duration 1 hour. The pressure dropped to 82 atm (21°), and 2,650 ml (0.12 mole) hydrogen was absorbed. After the usual working up, the reaction product was fractionated in vacuum: 1st fraction, b.p. 71.5° at 12 mm, n_D^{20} 1.5820, 4.7 g; 2nd fraction, b.p. 114-118° at 1 mm, n_D^{20} 1.5542, 8.0 g; 3rd fraction, b.p. 123-128° at 1 mm, n_D^{20} 1.5587, 2.5 g.

The 1st fraction is aniline; the 2nd fraction is 1-phenyl-2,5-dimethyl-4-methylaminopiperidine (yield 37%) [2].

Found %: N 12.70, 12.60. $C_{14}H_{22}N_2$. Calculated %: N 12.83.

The dipicrate of 1-phenyl-2,5-dimethyl-4-methylaminopiperidine melted at 185° (with decomposition) after recrystallization from alcohol-acetone.

Found %: N 16.46, 16.49. $C_{26}H_{28}O_{14}N_8$. Calculated %: N 16.56.

Reduction of 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone in presence of ammonia. A mixture of 7 g 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone (VII) (b.p. 90-94° at 4 mm, n_D^{20} 1.4748, 8 ml 25% aqueous ammonia and 7 ml methanol was hydrogenated, in presence of 1 g Raney nickel, under an initial hydrogen pressure of 102 atm (22°) at 150° for 1½ hours. The pressure fell to 92 atm (22°) and 1,300 ml hydrogen was absorbed. The base was salted out with sodium carbonate, extracted with ether and dried with sodium sulfate. Fractionation in vacuum (after removal of the ether) gave: 1st fraction, b.p. 50-51° at 1.5 mm, 2.2 g (40%); 2nd fraction, b.p. 78-79° at 1.5 mm, 1.5 g (21%); 3rd fraction, b.p. 156-161° at 1.5 mm, 1.5 g.

The 1st fraction is 1,2,3,5-tetramethyl-4-aminopiperidine (VIII), obtained in the form of a colorless, mobile liquid with an amine odor: n_D^{20} 1.4772, d_4^{20} 0.8984, MR_D 49.17; calc. 48.92.

Found %: N 17.12, 17.88. $C_9H_{20}N_2$. Calculated %: N 17.93.

The dipicrate of 1,2,3,5-tetramethyl-4-aminopiperidine melted at 220-221° (with decomposition) after recrystallization from aqueous alcohol.

Found %: N 18.09, 18.19. $C_{21}H_{26}O_{14}N_8$. Calculated %: N 18.24.

The 2nd fraction is 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidol (X), obtained in the form of a viscous, colorless liquid with an amine odor.

n_D^{20} 1.4812, d_4^{20} 0.9415, MR_D 60.57; calc. 60.20.
Found %: N 14.10, 13.85; OH 8.07, 8.65. $C_{11}H_{24}ON_2$. Calculated %: N 13.99; OH 8.49.

The picrate of the piperidol (X) melted at 86-88° (from alcohol).

Found %: N 16.30, 16.32. $C_{17}H_{27}O_8N_5$. Calculated %: N 16.32.

Reduction of 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone in presence of methylamine. A mixture of 7 g 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone (VII), 13 ml 25% aqueous methylamine solution and 10 ml methanol was hydrogenated, in presence of 1 g Raney nickel, under an initial hydrogen pressure of 100 atm (22°) at 140° for 2 hours. The pressure dropped to 89 atm (22°) and 1,350 ml hydrogen was absorbed. The mixture was worked up as in the preceding experiment. Vacuum fractionation gave 1st fraction, b.p. 52-53° at 1.5 mm, 2 g (33%); 2nd fraction, b.p. 78-79° at 1.5 mm, 1.5 g (21%); 3rd fraction, b.p. 158-161° at 1.5 mm, 1.5 g.

The 1st fraction is 1,2,3,5-tetramethyl-4-methylaminopiperidine (IX):

n_D^{20} 1.4804, d_4^{20} 0.9064, MR_D 53.41; calc. 53.72.
Found %: N 16.45, 16.25. $C_{10}H_{22}N_2$. Calculated %: N 16.45.

The dipicrate of 1,2,3,5-tetramethyl-4-methylaminopiperidine melted at 222° (with decomposition) after recrystallization from aqueous alcohol.

Found %: N 17.94, 18.02. $C_{22}H_{28}O_{14}N_8$. Calculated %: N 17.83.

The 2nd fraction is the above-described piperidol (X).

1,2,5-Trimethyl-4-acetylaminopiperidine (XI). 3 g 1,2,5-trimethyl-4-aminopiperidine (II, R = CH_3; R' = H) (b.p. 47° at 3 mm, n_D^{20} 1.4710) was mixed with 5 g acetic anhydride. At the conclusion of the exothermic reaction, the mixture was heated 30 minutes on a water bath. After cooling, the reaction mass was treated with 20% sodium hydroxide solution. The resultant oil was extracted with ether and dried with sodium sulfate. After removal of the ether, the residue crystallized. Two recrystallizations from benzine gave 2.5 g 1,2,5-trimethyl-4-acetylaminopiperidine (XI) with m.p. 142-143°; a white, fine powder, readily soluble in methanol, alcohol, acetone, ethyl acetate, dioxane, chloroform, carbon tetrachloride, benzene and hot benzine. Poorly soluble in water.

Found %: N 15.42, 15.22. $C_{10}H_{20}ON_2$. Calculated %: N 15.20.

1-Ethyl-2,5-dimethyl-4-acetylaminopiperidine (XIII). 1.5 g 1-ethyl-2,5-dimethyl-4-aminopiperidine (II, R = C_2H_5; R' = H) (b.p. 51-52° at 2.5 mm, n_D^{20} 1.4704) was mixed with 3 g acetic anhydride. The experimental procedure and working up of the products were as in the preceding preparation. Recrystallization from a mixture of benzine and benzene gave 1.3 g 1-ethyl-2,5-dimethyl-4-acetylaminopiperidine (XII) with m.p. 125°.

Found %: N 13.98, 13.90. $C_{11}H_{22}ON_2$. Calculated %: N 14.13.

SUMMARY

A study was made of the catalytic hydrogenation over skeletal nickel of 1-methyl-, 1-ethyl-, 1-propyl-, 1-n-butyl, 1-phenyl- and 1-cyclohexyl-2,5-dimethyl-4-piperidones (I) in presence of ammonia, methyl-, dimethyl-, ethyl-, propyl-, isopropyl- and cyclohexylamines, and also of ethanolamine, aniline and piperidine.

It was established that the reductive amination of the above 4-piperidones goes with facility only with ammonia and methylamine, when high yields are obtained of the corresponding 4-aminopiperidines. In this manner 11 4-amino- and 4-methylaminopiperidines (I) were synthesized and their hydrochlorides prepared for pharmacological investigation. In addition 2 acetylamino derivatives (XI) and (XII) were obtained.

By-products isolated from these reactions were two dipiperidylamines (III) and three secondary γ-piperidinic alcohols (IV).

Reductive amination of 1-alkyl-2,5-dimethyl-4-piperidones with higher primary amines and secondary amines could not be realized under the above conditions. In all cases, as illustrated by the example of 1,2,5-trimethyl-4-piperidone, 1,2,5-trimethyl-4-piperidol was formed instead of the expected 4-aminopiperidones.

Reductive amination, with the help of ammonia and methylamine, of 1,2,5-trimethyl-3-(dimethylaminomethyl)-4-piperidone (VII) is accompanied by hydrogenolysis of the side amino group with formation of 1,2,3,5-tetramethyl-4-aminopiperidines (VIII) and (IX), while in the case of 1-phenyl-2,5-dimethyl-4-piperidone, apart from formation of the corresponding 4-aminopiperidines, the piperidine ring is partly cleaved by hydrogen.

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Received February 2, 1955

Institute of Organic Chemistry, Academy of
Sciences USSR, and Lomonosov Institute of
Fine Chemical Technology, Moscow

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*T.p. = C. B. Translation pagination.

THE STRUCTURE OF GRAMICIDIN C

III. STUDY OF SOME PRODUCTS OF HYDROLYSIS OF GRAMICIDIN C

N. A. Poddubnaya and M. I. Kiselev*

It was shown in our laboratory by electrolytic reduction [1] and by investigation of copper complexes [2] that proline and phenylalanine are linked in the gramicidin molecule by an anhydride cyclic bond. It appeared necessary to obtain supporting evidence for this conclusion by direct isolation of this anhydride in the individual form.**

The native anhydrides of aminoacids have been isolated in numerous investigations [3,4] by autoclave treatment of protein and peptide structures in an acid medium. The isolation of prolyl-phenylalanyl anhydride after autoclaving confirms the presence of this anhydride in the structure of gramicidin. The method of autoclaving hydrolysis is perfectly suitable for application to gramicidin. The antibiotic, gramicidin C, is known to be extremely resistant to hydrolysis by strong acids. Thus, gramicidin C is not hydrolyzed by 25% sulfuric acid after treatment for 60-90 hours, nor by 22% hydrochloric acid after 36 hours [5], whereas any protein is broken down to aminoacids after hydrolysis with acids of the above concentrations for 18-20 hours, and sulfuric and hydrochloric acids exhibit no difference in activity. Gramicidin suffers no change [6] when hydrolysis is attempted with water at 1 atm (120°) for 30 minutes. In our experiments we applied a pressure of 10 atm and a temperature of 180°.

We know that the method of autoclave-hydrolysis was first proposed by N. D. Zelinsky and V. S. Sadikov [3,7] with the aim of destruction of protein and isolation of anhydrides from the hydrolyzates. Hydrolysis of the diketopiperazine ring goes with the greater facility the higher the concentration of acid, and with the greater reluctance the higher the position of the aminoacids in the homologous series. Concerning the anhydrization of a dipeptide, in the absence of acid this goes with the greater facility the higher the concentration of dipeptide and the greater its molecular weight. This process is considerably slowed down in an acid medium, and anhydrization ceases completely if the amount of acid taken for autoclave-hydrolysis is such that 1 atom of nitrogen corresponds to 1 mole acid. On the other hand, we can expect some cleavage of the anhydrides present to dipeptides and amino acids. In the autoclave-hydrolysis of gramicidin we therefore employed such a concentration of acid that the cleaved-off peptides were, as far as possible, neither hydrolyzed nor anhydrized.

We repeated the experiments of E. Abderhalden [4,8], M. Ludke [9] and N. D. Zelinsky and N. I. Gavrilov [10] on the hydrolysis of peptides and diketopiperazines under conditions of various pH values. We omit details of our experiments since they fully confirmed the observations of the authors cited. Experiments on hydrolysis of tripeptides are described below.

EXPERIMENTAL

Autoclave-hydrolysis of leucyl-glycyl-glycine and of alanyl-glycyl-glycine was carried out in sealed ampoules, each containing 0.2 g substance and 10 ml 1.5% sulfuric acid for 3 hours at 180° (10 atm). After hydrolysis the ampoules contained transparent, colorless solutions without deposit. The acid was removed with barium hydroxide and the solutions were evaporated (Table 1).

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* Deceased.

**Phenyl-alanyl-proline anhydride, present in the gramicidin molecule, is found in representatives of three different classes of compounds: proteins, alkaloids and antibiotics. It is evidently the commonest structural aggregate participating in the structure of natural products.

TABLE 1

Substance	After hydrolysis		Ratio of amino to total nitrogen (in %)		Note
	amino nitrogen (in mg) (Sorensen)	total nitrogen (in mg) (Kjeldahl)	original	after hydrolysis	
Leucyl-glycyl-glycine	10.43	14.90	33.40	70.00	Anhydride reaction negative for both tripeptides
Alanyl-glycyl-glycine	10.28	14.76	33.31	70.3	

The absorption spectra of the copper complexes of leucyl-glycyl-glycine and alanyl-glycyl-glycine were plotted before and after hydrolysis. As we see from the diagram, the maximum is shifted in the direction of longer waves, and this is further testimony to the hydrolysis of the peptide bond under these conditions and of formation of dipeptides.

Autoclave hydrolysis of gramicidin C and subsequent separation of the reaction products were effected according to the scheme:

Hydrolysis with 1.5% HCl or H_2SO_4 at 180°, 10 atm. $\xrightarrow{\text{Ionophoresis}}$
↗ Cathodic solution (peptides, aminoacids)
↘ Solution in middle cell (anhydrides)

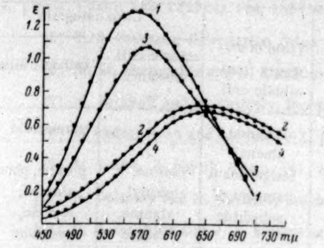
Autoclaving of an aqueous solution of gramicidin without addition of acid for periods of 1, 2, and 3 hours did not alter the substance. The melting point (277-281°) and absorption spectrum of the copper complexes (maximum 5.75 millimicrons) entirely corresponded to the original gramicidin: the "red" form of gramicidin was formed on standing with caustic alkali and copper (maximum 525 mμ). Autoclave-hydrolysis of 0.1 g gramicidin hydrochloride in 10 ml 1% HCl for 1-3 hours and 1.5% HCl for 1 hour likewise did not lead to change in the gramicidin. Solution occurred on autoclaving for 2 hours with 1.5% HCl, and a crystalline substance could be isolated from the middle cell after ionophoresis of the solution. After chromatographic analysis, the hydrolyzate of this crystalline substance gave three traces: proline, phenylalanine, and leucine. Ornithine is always absent from the chromatograms of the substance from the middle cell.

Four traces are usually found on the chromatogram of the substance from the cathodic solution: ornithine, di- and tripeptides. This mixture does not give a tripeptide reaction after hydrolysis in a sealed ampoule with 22% HCl, but after 48 hours hydrolysis a weak dipeptide reaction persists. Five aminoacids were detected on the chromatogram: proline, phenylalanine, valine, ornithine and leucine; also two peptides. These experiments indicate the difficulty of hydrolysis of peptides and the breakdown of the anhydride during autoclave-hydrolysis.

An anhydride with m.p. 212-216.5° was isolated from the middle zone of the electrophoretic cell after autoclave-hydrolysis of gramicidin with 1.5% HCl for 3 hours. Its hydrolysis was followed by development of two traces (proline and phenylalanine) on the chromatogram. The substance exhibits a very strong anhydride reaction, positive for pyrrole; it gives a yellow coloration, characteristic of proline anhydrides, with 3,5-dinitrobenzoic acid. It is readily soluble in water, acetone and methanol.

Found %: N (Kjeldahl) 10.9. $C_{14}H_{16}O_2N_2$. Calculated %: N 11.48.

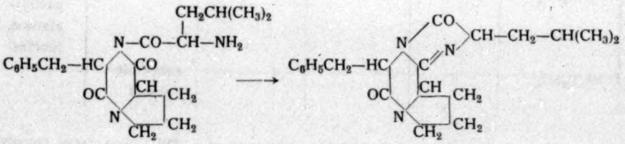
Hydrolysis with 1.5% sulfuric acid. 0.1 g gramicidin was dissolved in 15 ml sulfuric acid and heated in a sealed ampoule in an autoclave at 180° (10 atm) for 1, 2 and 3 hours. Dissolution was observed after hydrolysis for 3 hours but approximately 25% of the substance passed into the precipitate and, after recrystallization from aqueous alcohol, it had the form of lustrous needles which were identified as gramicidin sulfate (m.p. 292-294° with decomposition). The precipitate gives a violet color (biuret reaction) which changes to red on standing (like gramicidin hydrochloride). The distribution coefficient on the chromatogram corresponds to gramicidin (evidence of gramicidin base). After its hydrolysis with hydrochloric acid, five aminoacids are detected on the chromatogram in a medium of butanol-water-CH_3COOH (4:5:1): ornithin, proline, valine, leucine and



Absorption spectra of biuret complexes of tripeptides before and after autoclave-hydrolysis.
1) 0.01 M solution of Cu-leucyl-glycyl-glycine;
2) Cu-leucyl-glycyl-glycine after autoclaving;
3) 0.01 M solution of Cu-alanyl-glycyl-glycine;
4) Cu-alanyl-glycyl-glycine after autoclaving.

phenylalanine. Four traces are observed on the chromatogram after ionophoresis of the hydrolyzate of this substance in the middle cell: proline, phenylalanine, valine and leucine. Too low results were obtained in elementary analysis because the substance undergoes combustion with difficulty.

Hydrolysis with 3% sulfuric acid.* Gramicidin sulfate is not formed under these conditions but diketopiperazine is isolated in insignificant yield. Chromatographic analysis of the hydrolyzate of the middle cell gives three traces: proline, phenylalanine and leucine. It should be pointed out that in the case of incomplete hydrolysis we always found an anhydride consisting of the three amino-acids and remaining in the middle zone on electrophoresis. If we assume that proline-phenylalanine anhydride is linked to the tripeptide leucyl-ornithyl-valine, then it is possible that, due to the great facility of cleavage of ornithine which we always observed in our experiments, a second ring is formed according to the scheme:



Similar transformations were observed by A. Stoll [12] during formation of ergotamine. This may account for the absence of phoresis in the case of such compounds and its occurrence in the middle zone. We intend to make a closer study of these transformations.

Electrophoresis of the hydrolyzate of gramicidin. After numerous distillations of the hydrochloric acid or removal of the sulfuric acid with barium hydroxide, the hydrolyzate was subjected to electrophoresis in a three-chamber apparatus for 10-12 hours while a stream of CO_2 was passed through the cathodic cell [11]. Area of cathode 10.12 cm^2, continuous current density 98 ma /cm^2, current strength 100 ma. After completion of electrophoresis, the solution in the middle vessel was evaporated to dryness. If the middle-cell substance formed an oil, it was crystallized out of acetone solution with ether. The substance from the middle cell gave a very strong anhydride reaction and a negative ninhydrin reaction.

After completion of electrophoresis, the solution from the cathode chamber was evaporated in vacuum. In the case of incomplete hydrolysis, after electrophoresis and evaporation of the cathodic solution to dryness in vacuum, the solid was purified by dissolving three times in the minimum amount of alcohol and precipitating with ether. The solid gives a biuret reaction only with increased intensity in the long-wave region of the spectrum, but without a maximum. This points to the presence of dipeptides.

Open hydrolysis with 10% HCl. Taking into consideration the possibility of secondary formation of anhydrides during the process of autoclave-hydrolysis, we carried out hydrolysis under milder conditions. 50 ml 1% alcoholic solution of gramicidin was refluxed in a flask with 50 ml 10% HCl for 60 hours while boiling gently. The hydrolyzate was decolorized by digesting the solution with animal charcoal, after which the acid was driven off in vacuum. After six distillations of the hydrochloric acid and alcohol, the solid was dissolved in 10 ml water and subjected to ionophoresis for 20 hours at a current strength of 100 ma. The solution from the middle vessel

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*Gramicidin is completely hydrolyzed when heated with 5% sulfuric acid.

TABLE 2

Experiment No.	Acid concentration during hydrolysis	Duration of heating (hours)	Character of changes	Conditions of ionophoresis	Yield of substance from middle cell	Chromatogram	
						middle cell substance	cathodic solution
7	1.5% HCl	1	unchanged solid	9.8 ma/cm² (10 hrs)	anhydride absent	–	gramicidin
8	1.5% HCl	2	solution	9.8 ma/cm² (12 hrs)	insignificant amount of anhydride	proline, phenylalanine, leucine	proline, phenylalanine, leucine, ornithine
9	1.5% HCl	3	"	9.8 ma/cm² (12 hrs)	ditto	proline, phenylalanine,	ditto
10	1.5% H_2SO_4	3	large amount of solid (needles)	ditto	"	proline, phenylalanine, valine, leucine	"
11	3% H_2SO_4	3	solution	"	"	proline, phenylalanine, leucine	"
12	5% H_2SO_4	3	"	"	anhydride absent	–	"

gives a very strong anhydride reaction. Yield 0.01 g substance, m.p. 216°. Two traces (phenylalanine and proline) appeared on the chromatogram after its hydrolysis.

The experimental results on isolation of anhydride are set forth in Table 2. Experiments on the chromatogramming of the aminoacids were carried out not fewer than 3 times. Proline was developed with 0.4% solution of isatin in butanol by Acher's technique [13] (dark green trace on the chromatogram).

Consequently, both in the case of autoclaving and of open hydrolysis, the separation of proline-phenylalanine anhydride clearly indicates that it was originally part of the gramicidin molecule.

This confirms the investigation of the hydrolyzate of reduced gramicidin carried out by P. G. Ioanisiani [1] in which the chromatograms after reduction do not contain traces of phenylalanine and proline due to transformation of the diketopiperazine ring into piperazine.

SUMMARY

Proline-phenylalanine anhydride is found in the products of acid hydrolysis in an autoclave, thus demonstrating that this anhydride forms part of the original structure of gramicidin.

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Received April 19, 1955

Moscow State University

DISCUSSION

CONCERNING A PAPER BY N. RIL AND G. ORTMAN

A. Bundel

In the June and July issues of Journal of General Chemistry for 1955 (Numbers 6 and 7) papers were published by N. Ril and G. Ortman on "Participation of oxygen in the formation of zinc sulfide luminophores" [1] and "Chemistry of formation of luminescence centers in zinc sulfide luminophores" [2]. They describe with extreme brevity new experiments by the authors, and on the basis of the results obtained, they put forward models of the centers of luminescence in ZnS luminophores.

The importance of the problem which N. Ril and G. Ortman occupied themselves with, and the large number of existing publications on the subject, should have induced the authors to give an exhaustive account of their experiments and to submit quantitative data for the influence of various factors on the luminescence of ZnS. Instead of this, they only report the results of qualitative observations and do not always convincingly interpret them. We touch below only on the more conspicuous errors of both papers.

1. The authors used insufficiently pure preparations of zinc sulfide obtained by precipitation with hydrogen sulfide. According to their data, the non-ignited sulfide contained up to 3.5% $ZnSO_4$ or 2.4% $ZnCl_2$; after ignition at 850° it was not pure ZnS since the content of Zn + S fell to 97.2%, while "the deficit of sulfur in relation to zinc" reached 8.3%.

For experiments on activation with copper at low temperatures, zinc sulfide ignited at 1200° was used. It was characterized only by the statement that its intensity of luminescence was "negligibly small". This can evidently be associated with the far-reaching oxidation of the preparation, since preparations with good luminescence are obtained by ignition in a nitrogen atmosphere at 1200°. Thus, according to the data of Bube [3], the brightness of the wurtzite modification,obtained at 1200° with 1% NH_4Cl, is 30% of the brightness of the preparation ignited at 900°; again, according to A. I. Rusanova [4], the preparation with 5% NaCl has 40% of the brightness of ZnS ignited at 950°.

In one of the preceding papers [5], in which N. Ril describes similar experiments with use of Cu, the luminescence spectrum of the original ZnS, ignited at 1200° in the air, is presented. The maximum lies at about 510 mμ, i.e. close to that in zinc oxide or oxysulfide. Results obtained with preparations of such indeterminate composition are applied to zinc sulfide; it is natural that the conclusions reached in this fashion cannot be reliable.

2. In the investigation of the influence of ignition in an atmosphere of dry HCl on the luminescence of ZnS, Ril and Ortman concluded that HCl is a powerful desulfurizing agent for ZnS, surpassing even hydrogen in this respect. This conclusion is later used as a basis for the authors' proposed model of the luminescence centers. The basis for such a conclusion is their observation of the graying of ZnS after ignition in HCl. The authors write: ". . . a gray color visible to the eye" (page 1297); ". . . ignition of pure ZnS in dry HCl vapor leads to the separation in the zinc sulfide crystals of free zinc in quantity sufficient for visual observation". No evidence at all is given to support the statement that the change of color of ZnS is actually bound up with the separation of zinc. Decolorization does not take place when such preparations are treated with hydrochloric acid. It is therefore possible that the color is not associated with the separation of "free zinc". However, the authors put forward another suggestion, namely, that "free zinc" is deposited inside the crystals. No suggestions are made as to the mechanism of separation of zinc in presence of HCl. The only comment is: "The mechanism of

formation of free zinc in presence of excess of free HCl is obscure and requires special study, but it appears less remarkable when we recall that free Zn is formed inside the sulfide crystals, i.e. not in direct contact with HCl" (page 1296). It is impossible, however, to regard such an argument as convincing proof of the validity of the far-reaching conclusions of N. Ril and G. Ortman. The insolubility of the gray substance in acid is due more likely to the substance being an impurity. It should be pointed out that the ignition of sulfide luminophores in HCl has been often described [6,7],but no mention has been made of the formation of dark colored products.

3. Ril and Ortman also observed the appearance of a dark color in zinc sulfide when ignited in vacuum at 900-1050°. In this case again, the dark substance does not dissolve in hydrochloric acid, but this fact did not prevent the authors from describing it as "free zinc" evolved as a result of thermal dissociation of ZnS (page 1291). No evidence is adduced that the gray substance is zinc. The separation of free zinc as a separate phase is impossible, however, during thermal dissociation of ZnS, since the vapor tension of Zn at temperatures of 900 to 1000° [8] is at least 10^4 times higher than the vapor tension of zinc in the products of dissociation of ZnS [9].

4. N. Ril and G. Ortman assert [1] that the formation of an inactive luminophore with a blue luminescence requires the presence of oxygen. This conflicts with the results obtained hitherto. As a rule, normal inactive luminophores are obtained on ignition in nitrogen (Bube, Leverents, Kroger, Fonda, Grillo, Shtrek, Smit, Rusanova, Moskvin and many others). The suggestion that the experimental procedure was faulty in these investigations is not convincing. It would have been expected that Ril and Ortman would have provided substantial proof of such a striking fact which conflicted with previous experimental data. However, neither in their drawing of the apparatus for ignition in nitrogen, nor in the short description of the experimental set-up are there any indications of devices for feeding oxygen into the system and for its accurate proportioning. They write: "If the slightest trace of oxygen is introduced into the system (in quantity such that the number of oxygen atoms is of the same order as the number of centers of luminescence in the zinc sulfide), then a blue luminescence is at once developed".

The impression is created that the authors' conclusion about the role of oxygen is reached, not on the basis of accurate experiments on the dependence of the luminescent properties of ZnS on the amount of oxygen introduced, but on the basis of arbitrary interpretation of experiments in which, for reasons not clear to the authors, luminescing preparations were obtained. If a more exhaustive investigation had been carried out, it would not have been necessary to seek for confirmation of the suggested role of oxygen in indirect considerations, as is done by the authors on page 1065 in connection with the ignition of ZnS + NaCl in H_2S: "Due, however, to the absence of oxygen, the blue luminescence was not developed in spite of the presence of HCl. This conclusively removes any doubt that when working in vacuum the essential factor is the absence of action of oxygen as a promotor of formation of HCl".

It remains to express regret that N. Ril, who has contributed so much to the study of zinc sulfide luminophores, should in recent publications have introduced such unfortunate errors.

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Received December 16, 1955

EDITORIAL NOTE

In the paper by A. F. Kapustinsky and K. B. Yatsimirsky on "Lattice energy of salts formed with ions with an eight-electron external shell" [JGC 26, No. 4, 941 (1956)(C.B. translation p. 1069)] an error occurred due to the authors' fault.

Equations (4), (5) and (5a) should read as follows:

$$\rho = 0.345 - 0.00870(r_K + r_A)^2, \qquad (4)$$

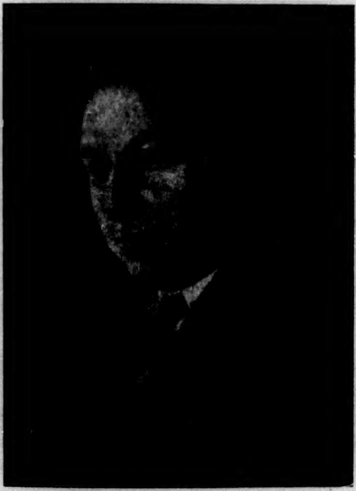
$$U = 287.2\,\frac{\Sigma n\, Z_K \cdot Z_A}{r_K + r_A}\left[1 - \frac{0.345 - 0.00870(r_K + r_A)^2}{r_K + r_A}\right], \qquad (5)$$

$$U = 287.2\,\frac{\Sigma n \cdot Z_K \cdot Z_A}{r_K + r_A}\left[1 - \frac{0.345}{r_K + r_A} + 0.00870\,(r_K + r_A)\right]. \qquad (5a)$$

TO THE MEMORY OF M. V. LIKHOSHERSTOV

A. A. Petrov

Professor, Doctor of Chemical Sciences Mikhail Vasilevich Likhosherstov, widely known for his work on the chemistry of haloamides and on methods of halogenation, passed away in Moscow on July 25, 1950.



M. V. Likhosherstov was born in the village of Teterevino, Belgorodsky region, Kyrskaya district, on September 1, 1902 in a peasant family. After leaving school in 1919, he entered the Belgorodsky State Institute of Education. Leaving this institute in 1922, he transferred to the chemical department of the physicomathematical faculty of Voronezh University where he completed his training in 1926. He stayed on as a research assistant and was granted a fellowship in October 1926 in the department of organic chemistry under Prof. A. D. Bogoyavlensky. After graduating as a fellow (March 1930), M. V. continued working at Voronezh University until July 1942 – 1 year as assistant lecturer, 5 years as lecturer, from 1935 as professor, and from 1939 as director of the department of organic chemistry. His doctoral dissertation on "Investigations in the field of organic N-halo derivatives" was successfully defended in 1940 and he was honored by the award of the prize of the All-Union Mendeleev Chemical Society.

Simultaneously with his main work in the university, Mikhail Vasilevich also worked in other higher educational institutes in Voronezh (the Agricultural Institute, the Institute of Education, the Institute of Chemical Technology). He worked in the latter until 1942 and resumed work there as state professor in 1945. From September 1948 until the day of his death, Mikhail Vasilevich directed the department of organic, biological and physical chemistry at the Institute of Technology of the Fish Industry at Astrakhan.

During the period of his scientific activity, Mikhail Vasilevich carried out 56 scientific investigations on organic chemistry. He worked in the field of the chemistry of N-halo derivatives, aromatic amines and phenols, chlorohydrins, oxides and their derivatives, ethers and esters of halohydrins, dioxane homologs, and furan derivatives. He developed new methods of halogenation and thiocyanation of organic compounds. Interesting studies were carried out on the by-products of synthetic rubber and on the synthesis of new solvents.

The main achievements of Mikhail Vasilevich were in connection with new methods of halogenation and thiocyanation of organic compounds with the help of haloamides. He investigated the application of fatty haloamides to the halogenation and thiocyanation of mainly aromatic compounds.

The reactions have the following general course (illustrated for dichlorourea):

$$2ArH + 2KHlg + (NHCl)_2CO \longrightarrow 2ArHlg + 2KCl + (NH_2)_2CO.$$

In this way it is possible to successively introduce identical or different halogens, as well as the thiocyano group, into aromatic compounds. Investigation of the mechanism of this reaction showed that the haloamides here act as oxidizing agents.

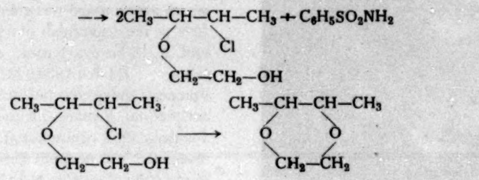
Fatty and aromatic N-haloamides were later used for the synthesis of chlorohydrins and their ethers according to the scheme (where R = H, Alk, Ar or Acyl):

$$>C{=}C< + ROH + >N{-}Hlg \longrightarrow >C(OR){-}CHlg< + >NH.$$

In this fashion M. V. was able to prepare, apart from diverse halohydrins, their ethers and esters, as well as phenol ethers. Synthesis of the latter by the scheme mentioned is of great interest for study of the mechanism of halogenation of phenols.

A series of oxides, glycols, and glycol monoethers was obtained from chlorohydrins. M. V. developed an interesting method of synthesis, on the basis of the reaction in question, of derivatives of dioxane according to the scheme (illustrated for pseudobutylene and ethylene glycol):

$$2CH_3{-}CH{=}CH{-}CH_3 + 2CH_2OH{-}CH_2OH + C_6H_5SO_2NCl_2 \longrightarrow$$



Other methods were also proposed by M. V. for the preparation of ethers of chlorhydrins: direct addition of alkyl hypochlorites to olefins and the so-called alkali method. M. V. suggested the utilization of esters of chlorohydrins as solvents.

The work of M. V. on addition of haloamides to unsaturated compounds and on the condensation of N-haloamides with thioethers is of great interest. Depending upon the nature of the amide radical, the latter reaction goes by one of the following schemes:

$$R_2S + AlkCONHCl \longrightarrow [R_2S{-}NHCOAlk]Cl,$$
$$R_2S + ArCONHCl \longrightarrow R_2S \longrightarrow NCOAr + HCl$$

Special mention is merited by his work on the by-products of the synthetic rubber industry. Mikhail Vasilevich was the first to discover esters and phenols and their ethers in these by-products. Later studies by M. V. were on the utilization of a by-product of the hydrolysis industry – furfural. Starting from furfural he developed a method of synthesis of furacrolein, furallyl alcohol and esters of ketopimelic acid.

Throughout the period of his scientific activity, Mikhail Vasilevich attracted a large number of young scientific workers, more than 20 of whom collaborated with him in researches. Twelve doctoral candidates were trained under the direction of Mikhail Vasilevich. He was a superb lecturer, capable of lucidly presenting the most difficult problems of organic chemistry without sacrificing accuracy of his exposition; this gift gained him the deserved affection of the student body.

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*T.p. = C. B. Translation pagination.

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